1985

Bimetallic Tungsten Carbonyl Complexes

Jin-Guu Wang
Eastern Illinois University

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BIMETALLIC TUNGSTEN CARBONYL COMPLEXES

(TITLE)

BY

Jin-Guu Wang

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

MASTER OF SCIENCE IN CHEMISTRY

IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY
CHARLESTON, ILLINOIS

1985

YEAR

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ABSTRACT

Title of Thesis: Bimetallic Tungsten Carbonyl Complexes

Name: Jin-Guu Wang

Thesis directed by: Dr. Richard L. Keiter

Two heterobimetallic complexes, $[(CO)_4W(PPh_2CH_2CH_2PPh_2)_2MCl_2]_n$ (M = Pd or Pt), were prepared from the reaction of trans-$W(CO)_4(\eta^1\text{-}PPh_2CH_2CH_2PPh_2)_2$ with $M(COD)Cl_2$ (COD = cyclooctadiene). A trans arrangement about tungsten was found for both the palladium and platinum complexes. The square planar palladium center was shown to have a trans geometry in solution while a cis arrangement for the platinum moiety was observed. Far infrared studies indicated a mixture of cis and trans isomers in the solid state for the platinum center. The solubility of the bimetallic complexes precluded solution molecular weight studies and as a result the value of n has not been determined.

Preliminary results for the reaction of trans-$W(CO)_4(PPh_2CH{=}CH_2)_2$ with $Pt(PPh_2H)_2Cl_2$ in the presence of base lead to unidentified products. This method does not appear promising for the preparation of bimetallic compounds.

The reaction of $W(CO)_6$ with $PPh_2CH{=}CH_2$ in n-butanol

in the presence of $NaBH_4$ yielded the starting material, trans-$W(CO)_4(PPh_2CH{=}CH_2)_2$ in 31% yield. It appears that the less soluble trans isomer precipitates from a solution containing an equilibrium mixture of cis and trans isomers. The vinyl complex was converted to trans-$W(CO)_4$-$(\eta^1\text{-}PPh_2CH_2CH_2PPh_2)_2$ by allowing it to react with PPh_2H in the presence of potassium t-butoxide. Some isomerization and cyclization led to the formation of $W(CO)_4$-$[PPh_2CH_2CH_2CH(PPh_2)CH_2PPh_2]$, obtained as minor product.

It was not possible to prepare $W(CO)_4(PPh_2H)_2$ from the reaction of $W(CO)_6$ with PPh_2H in the presence of $NaBH_4$. This reaction led to the formation of $(OC)_4W$-$(PPh_2)_2W(CO)_4$, $(CO)_4W(PPh_2)_2W(CO)_3PPh_2H$ and an unidentified product.

The reaction of fac-$W(CO)_3(PPh_2CH{=}CH_2)_3$ with PPh_2H in the presence of base gave $W(CO)_3(\eta^2\text{-}PPh_2CH_2CH_2PPh_2)$-$(\eta^1\text{-}PPh_2CH_2CH_2PPh_2)$ instead of fac-$W(CO)_3(\eta^1\text{-}PPh_2CH_2CH_2$-$PPh_2)_3$.

Proton decoupled phosphorus-31 NMR and infrared spectra, along with elemental analyses, were used to determine the structures of the compounds. Computer methods were used to simulate NMR spectra of trans-$W(CO)_4$-$(\eta^1\text{-}PPh_2CH_2CH_2PPh_2)_2$, $(CO)_4W(PPh_2CH_2CH_2PPh_2)_2PtCl_2$, and $W(CO)_3(\eta^2\text{-}PPh_2CH_2CH_2PPh_2)(\eta^1\text{-}PPh_2CH_2CH_2PPh_2)$.

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ACKNOWLEDGEMENT

I would like to express my sincere gratitude to Dr. Keiter whose guidence and generous help have made my research a wide experience, and have made the writting of this thesis possible.

To Mrs. Ellen A Keiter, who helped in obtaining the P-31 NMR spectra of the compounds discussed in this thesis. My sincere thanks also go to Dr. Giles Henderson for helping me in constructing the computer program for simulating NMR spectra and allowing me to use his program for diagonalizing the Hamiltonium matrix.

Finally, I would like to greatly thank my parents who have been supportive in all my undertakings.

CHAPTER I

INTRODUCTION

Over the past twenty-five years, the development of homogeneous catalysis has had a major impact on the growth of organometallic chemistry. Carbonyl complexes have received particular attention because of their industrial use in hydroformylation and because of the current interest in the Fischer-Tropsch reaction. The hydroformylation reaction, which converts an olefin, carbon monoxide and hydrogen gas into aldehydes, is used to produce six billion pounds of butanal annually.[1]

$$CH_3CH{=}CH_2 + CO + H_2 \xrightarrow{Co_2(CO)_8} CH_3CH_2CH_2CHO$$

The Fischer-Tropsch reaction, which involves the catalytic reductive polymerization of carbon monoxide, is not at present economically useful. It is used in South

$$CO + H_2 \xrightarrow{\text{metal oxides}} \text{hydrocarbons}$$

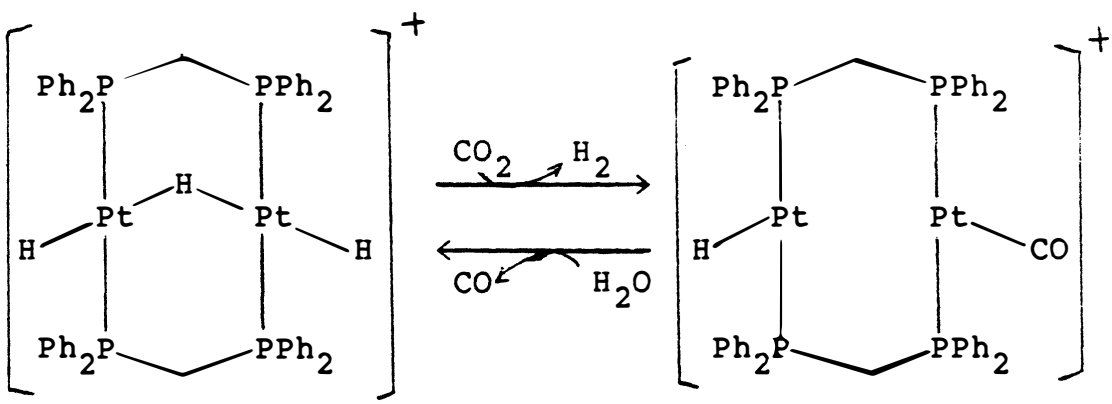
Africa where coal is abundant. The process as currently operated requires high temperatures and utilyzes heterogeneous catalysts which give poor selectivity. As a result of these limitations both industrial and academic scientists have sought homogeneous catalysts which give

good selectivity and function at a low temperature.

It has been suggested that a vacant coordination site is the single most important property of a homogeneous catalyst. A catalyst must have carefully balanced bonding properties such that it can accept the desired ligand and yet does not accept an alternative but nonreactive ligand instead.

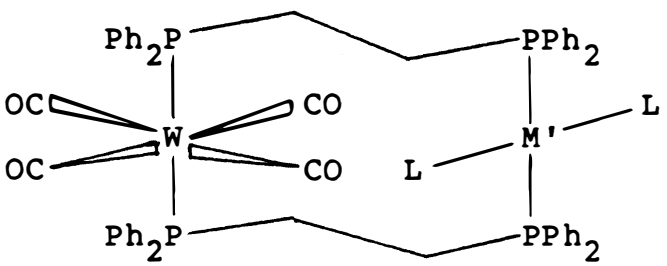
Bimetallic complexes contain two metal atoms which may be of the same or different elememts. In some instances bimetallic complexes may be more specific for catalysis than monometallic complexes and these characteristics may be enhanced by carefully choosing the ligands and metals.

For both theoretical and practical reasons, the preparation of compounds which contain two metals has received considerable attention.[2,3,4] For example, the water gas shift reaction, $CO + H_2O \rightleftharpoons CO_2 + H_2$, can be catalyzed by a platinum A-frame Complex.[1]

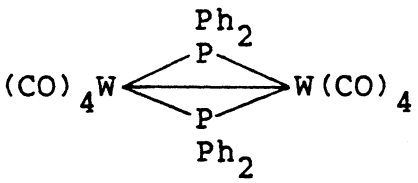


The purpose of our research has been to synthesize heterobimetallic carbonyl complexes, which in principle

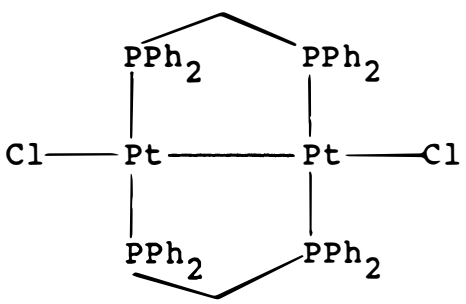
can function as homogeneous catalysts. Our idea has been to create complexes of the type, $(OC)_4W(PPh_2CH_2CH_2PPh_2)_2$-$M'L_2$, in which W is at an octahedral center and M' is at a square planar center. The metal, M, could add hydrogen gas in an oxidative-addition type reaction and conceivably the activated hydrogen could transfer to a bound CO of the metal M.



Many groups have previously synthesized complexes which contain more than one metal. Metal clusters with pronounced M-M bonding are common. Many of these complexes exist in which metal atoms are held together by various bridging ligands. Most common are those in which two metal atoms are held together by a R_2P-, (phosphido), or a $Ph_2PCH_2PPh_2$ (dpm) bridge.[1,5]

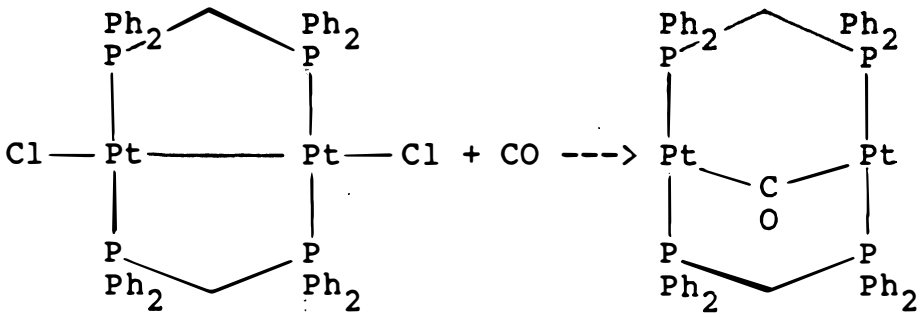


(a)



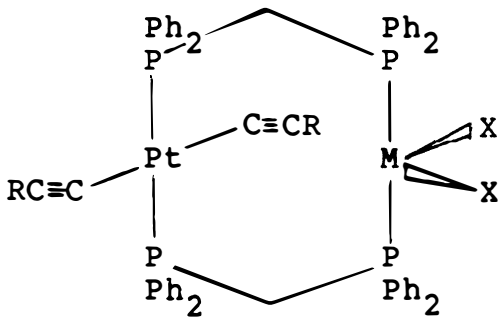
(b)

These kinds of complexes have been of particular interest because the two metal atoms are held sufficiently close to allow simultaneous interaction of both metal atoms with a small molecule. For example, CO reacts readily with (b) to form a complex containing a bridging carbonyl group.[1]



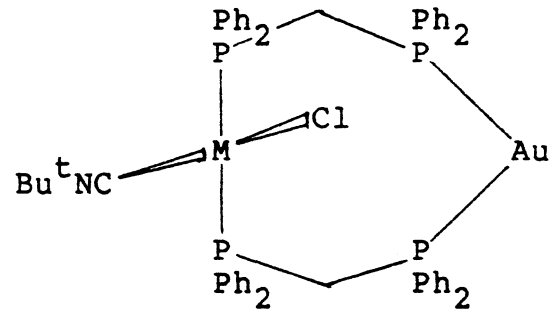
(b)

During the past few years, Shaw and coworkers have successfully synthesized many heterobimetallic complexes containing double dpm bridges. A series of heterobimetallic complexes of palladium and platinum with silver, gold, rhodium, iridium, mercury, molybdenum and tungsten were reported.[6,7,8,9]



M = Rh, Ir, Ag, Au, Cd Hg, or W

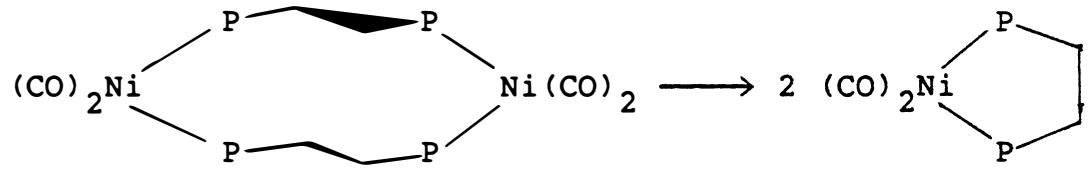
X = Cl, I.



M = Pt or Pd

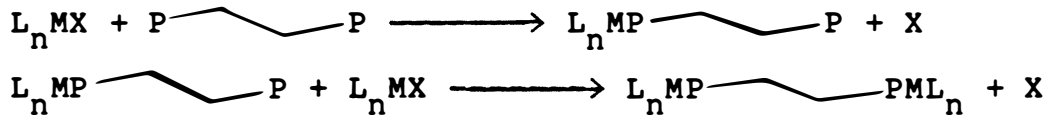
In our work, we have chosen $Ph_2PCH_2CH_2PPh_2$, dpe, to function as a bridging ligand. The separation between the two phosphorus atom of dpe is 4.5 Å.[10] When the two phosphorus atoms of both dpe molecules coordinated to two different metals to form a double bridges bimetallic complex, the ligands of the two metals are brought into close proximity.

Bridged and chelated complexes of dpe have been known for nearly as long as the ligand itself. Unidentate dpe complexes[11] are much rarer and in general have been synthesized unintentionally rather than by design. In part this is true because the usual methods of synthesis of carbonyl phosphine complexes involve substitution of one ligand for another, reactions in which vacant coordination sites become availabe to invite coordination of dangling phosphines. If conditions are harsh, chelation is the principal result because two coordination sites on the same metal often are exposed and because bridged products are unstable with respect to chelation.[12]



On the other hand, under the mild conditions typical for substitution of an easily displaced ligand, the desired product, which is also a ligand, may react further to

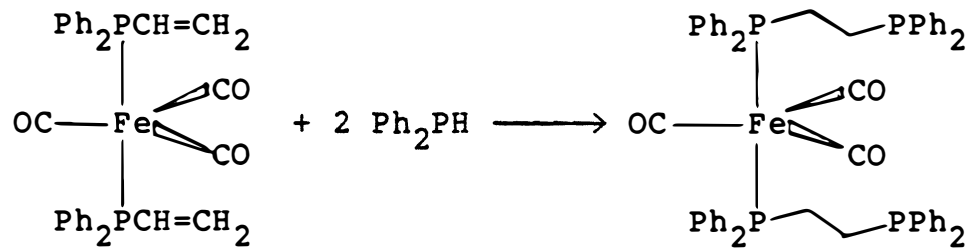
give a bridged product.

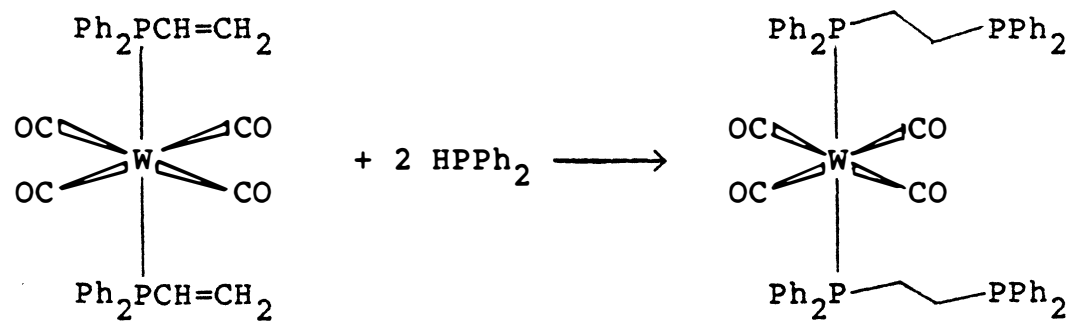


Substitution reactions and their inherent weakness may be avoided by using addition reactions which proceed without creating vacant coordination sites. The reaction of $Fe(CO)_4(PPh_2CH{=}CH_2)$ or $M(CO)_5(PPh_2CH{=}CH_2)$ (M= Cr,Mo,W) with PPh_2H in the presence of base or free radical affords $Fe(CO)_4(\eta^1\text{-dpe})$ or $M(CO)_5(\eta^1\text{-dpe})$ in good yield.[13]

$$M(CO)_n(PPh_2CH{=}CH_2) + Ph_2PH \longrightarrow M(CO)_n(\eta^1\text{-}PPh_2Ch_2CH_2PPh_2)$$

These products are stable with respect to chelation under the mild conditions (refluxing THF) of the reaction. The success of this approach as a method for preparing uni-

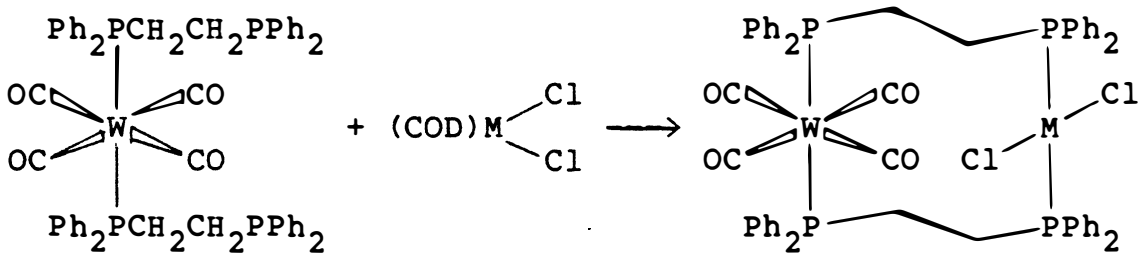




dentate dpe complexes is further illustrated by the synsynthesis of $Fe(CO)_3(\eta^1\text{-dpe})_2$ and $M(CO)_4(\eta^1\text{-dpe})_2$ (M = Cr, Mo, W).[13,14]

Because of the excellent thermal stability of these complexes, chelation does not occur. These complexes contain dpe molecules bonded as unidentate ligands, which suggess that they may possess a rich chemistry as chelating ligands.

In this thesis the reactions of Pt(II) and Pd(II) with $W(CO)_4(\eta^1\text{-dpe})_2$ have been examined.



M = Pd, Pt

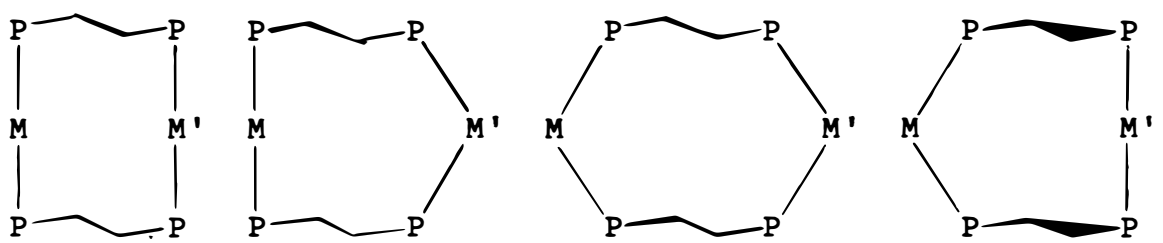
COD = cyclooctadiene

It is known the reaction of chelating phosphine ligands with $PtCl_4^=$ or $PdCl_4^=$ often leads to Magnus-type $[M(L\text{-}L)_2]MX_4^=$ complexes, which are of limited solubility in most solvents.[15] In addition the poor solubility of MX_2 salts in all solvents inhibits their use in direct reactions with phosphine ligands. Therefore, an alternative method was needed for synthesizing the tungsten-palladium or tungsten-platinum heterometallic complexes. A fast reaction, without Magnus salt formation, occurs when a

neutral ligand is displaced by the phosphine from $(COD)MCl_2$ (where M=Pd,Pt; COD=cyclooctadiene).[16]

$$MCl_4^{=} + COD \longrightarrow (COD)MCl_2 + 2\ Cl^-$$

Several different reaction products are possible when <u>trans</u>-$(OC)_4W(\eta^1\text{-dpe})_2$ is allowed to react with a square planar complex by a substitution reaction. There are four potential structural isomers for a nonpolymeric chelated product: <u>trans</u>-<u>trans</u>, <u>trans</u>-<u>cis</u>, <u>cis</u>-<u>cis</u>, <u>cis</u>-<u>trans</u>.

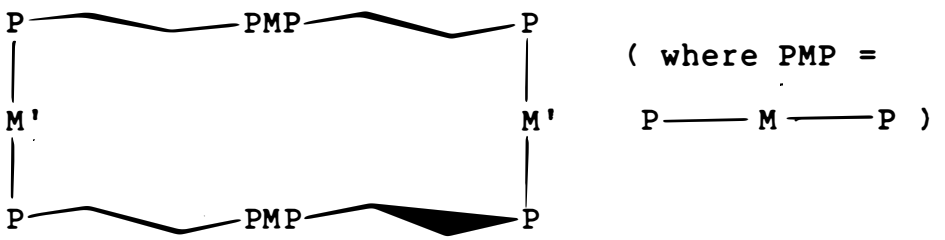


<u>trans</u>-<u>trans</u> (A) <u>trans</u>-<u>cis</u> (B) <u>cis</u>-<u>cis</u> (C) <u>cis</u>-<u>trans</u> (D)

It is possible that polymerization may be more favorable than the formation of any of the 10-membered rings shown above. The conclusions of some published literature[17,18,19] show that the stability of chelated complexes depend on ring size. Favorable conformation and entropy effects appear to make large rings more stable than those of intermediate size. It has been reported that although ditertiary phosphine, $R_2P(CH_2)_nPR_2$, of medium length backbones (n=5-8) many give dimers, trimers, or polymers, large chains phosphines (n=12) often

form trans monomeric complexes.[17] The free energy difference between a large chelate ring and an open chain polymer appears to be small since many examples of each have been described. If polymers are not thermodynamically favored in our systems, their formation for kinetic reasons can be avoided or greatly minimized by performing the reactions under dilute condition.

Even very large-ring complexes must be considered as possible products. Shaw et al. have reported a stable complex, <u>trans</u>-$PdCl_2[^tBu_2P(CH_2)_{10}PBu^t_2]$ which contains a 26-atom ring.[20] By analogy, a 20-atom ring complex (and its many isomers) as a possible product from our reactions, can be postulated.



There are several important reasons why we choose <u>trans</u>-$M(CO)_4(\eta^1\text{-dpe})_2$ to coordinate to a metal with a preference for square planar geometry. From a stereochemical point of view, it is clear that coordination of our ligand to an octahedral center would only be possible if a cis arrangement were assumed. A trans arrangement would be prevented by close approach of the ligands which would lie between the two metals. However, both cis and trans

coordination may be possible with a square planar geometry because of reduced steric repulsion between ligands of the two metal atoms of the bimetallic complex.

If a trans-trans arrangement is possible, it would be a tight fit, because loss of entropy due to restricted flexibility in the carbon backbones of the ligands could render this structure unfavorable. If a trans-trans geometry is not favorable , it is likely that intramolecular isomerization to trans—cis (B), cis—cis (C), or cis—trans (D) complexes will occur. The possible structure will depend on the energy barrier of the isomerization reaction with respect to each metal center in this situation. Of course, it is also possible that several isomers exist in equilibrium in solution.

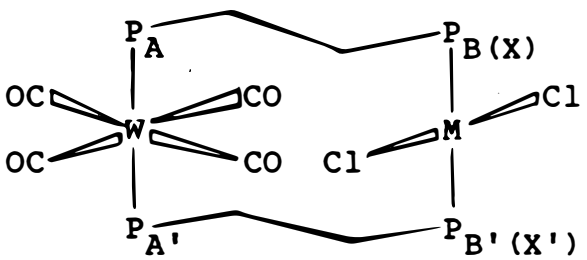
In addition to the first approach, which uses <u>trans</u>-$(CO)_4W(\eta^1\text{-dpe})_2$ as a starting material, there is another approach to bimetallic complexes that has been examined in our work. Based on the great success of the base-catalyzed addition of P-H bonds to vinyl groups, it was supposed that the following two reactions may take place.

$$\underline{\text{trans}}\text{-}(CO)_4W(PPh_2CH{=}CH_2)_2 + \underline{\text{cis}}\text{-}M(Ph_2PH)_2Cl_2 \xrightarrow[THF]{(CH_3)_3COK} (CO)_4W(PPh_2CH_2CH_2PPh_2)_2MCl_2$$

$$\underline{\text{cis}}\text{-}(CO)_4W(Ph_2PH)_2 + \underline{\text{cis}}\text{-}M(Ph_2PCH{=}CH_2)_2Cl_2 \xrightarrow[THF]{(CH_3)_3COK} (CO)_4W(PPh_2CH_2CH_2PPh_2)_2MCl_2$$

It is possible that the addition reaction approach would minimize polymerization.

The phosphorous spin system for the bimetallic complex is expected to be AA'BB' or AA'XX'.



where M = Pt, Pd

As part of this thesis, P-31 spectra were computed for the purpose of simulating the obtained experimental spectra.

CHAPTER II

RESULTS AND DISCUSSION

The synthesis of the basic starting material trans-$W(CO)_4(PPh_2CH2=CH_2)_2$, was less straight-forward than had been predicted. The traditional method of preparing a disubstituted tungsten carbonyl complex involves heating $W(CO)_6$ with the appropriate tertiary phosphine at 160^0C in diglyme, $CH_3OCH_2CH_2OCH_2CH_2OCH_3$.

$$W(CO)_6 + 2PR_3 \xrightarrow[160^0C]{\text{diglyme}} W(CO)_4(PR_3)_2 + 2\ CO$$

In addition to low yields (29 %) obtained by us when the phosphine is $Ph_2PCH=CH_2$, several other disadvantages were found in this reaction. At the temperature employed, $W(CO)_6$ sublimes from the reaction mixture and is deposited in the condenser. Thus it is difficult to maintain the desired stoichiometric ratio throughout the reaction. The principal problem, as perceived in the early stages of this work, arises from the mixture of products obtained under the harsh condition of the reaction. A mixture of cis and trans isomers, cis-$W(CO)_4(PPh_2CH=CH_2)_2$ and trans-$W(CO)_4(PPh_2CH=CH_2)_2$ usually resulted. It was our thought that the cis/trans mixture occured because the reaction was thermodynamically controlled at high temperatures.

In an attempt to increase yields, avoid $W(CO)_6$ sublimation, eliminate solvent drying and obtain pure trans isomer we investigated a reaction reported in 1970 by Chatt.[21]

$$W(CO)_6 + 2\ PR_3 \xrightarrow[EtOH]{NaBH_4} (OC)_4W(PR_3)_2 + 2\ CO$$

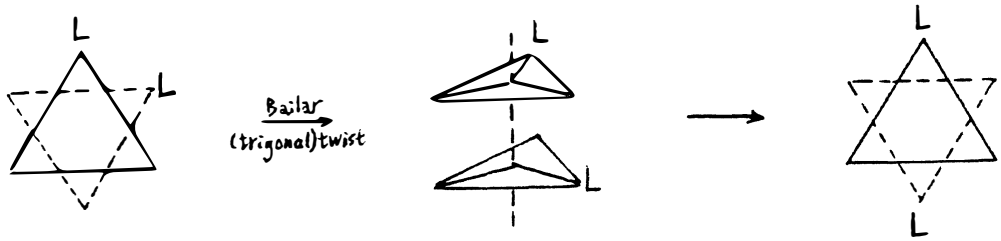
The reaction in ethanol for $PPh_2CH{=}CH_2$ led to new a complication. In addition to cis and trans $W(CO)_4(PPh_2CH{=}CH_2)_2$, trisubstituted fac-$W(CO)_3(PPh_2CH{=}CH_2)_3$ was also obtained. Recrystallization and column chromatographic technique were used in an attempt to separate the mixture but not successfully. It was found that the facial complex could be obtained as the only product if an excess amount of $PPh_2CH{=}CH_2$ was used. When the reaction was carried out in n-butanol, a mixture of cis and trans isomers resulted. Fortunately, pure trans isomer slowly precipitated, due to its lower solubility, from the filtrate when it was allowed to stand at room temperature for several days.

The $NaBH_4$ approach was an improvement over the diglyme method. Sublimation problems were eliminated and solvent preparation wascless tedious. Yield was improved (32 %), although only slightly. The method, however, did not eliminate the formation of cis/trans mixtures. Recent work reported in the literature by Darensbourg[22a] and by Howell[22b] allows us to explain our observation. According to their conclusion it is be-

lieved that there is a thermodynamic preference of either the cis or trans isomeric form of $M(CO)_4L_2$ depending on both the electronic and steric properties of L (the nature of the lone pair electron on the phosphorus atom and the bulk of the group attached to the phosphorus atom). A sterically demanding ligand will lead to the trans isomer as the more thermodynamically stable species while a ligand with a small cone angle will lead to the cis isomer as the most stable since electronic effects will dominate. The ligand, $PPh_2CH=CH_2$, is intermediate in size and a mixture of cis and trans isomers results. The trans isomer is dominant, indicating that steric factors are more important than electronic factors for this ligand.

Isomerization of cis and trans isomers is a facile process and proceeds even at room temperature. Quantitative studies have been reported on the cis $\rightleftharpoons$ trans isomerization of $Mo(CO)_4(PR_3)_2$ (R = Me, Et, Bu, and Ph) complexes,[23] $M(CO)_4$ (^{13}CO)(PR_3) (M = Cr, R = OMe, Me, Et, i-Pr) complexes[24] and $M(CO)_4L_2$ complexes (M = Cr, Mo, W; L = PBu_3, $P(OMe)_3$, $P(OPh)_3$)[25]. Isomerization can occur by both dissociation and intramolecular processes. If the ligand is bulky, dissociation occurs to give a five-coordinate square pyramidal complex which undergoes pseudorotation to give a trigonal bipyrmidal species which may accept the dissociated ligand to give the isomerized product. In other instances studies show that isomerization proceeds by a nondissociative intramolecular pro-

cess, perhaps involving a Bailar twist mechanism.



In our $NaBH_4$ reaction, the pure trans isomer slowly precipitated from the n-butanol reaction mixture. This can be explained by assuming that an equilibrium mixture of cis and <u>trans</u>-$W(CO)_4(PPh_2CH{=}CH_2)_2$ existed in solution and that the more insoluble trans species precipitated from solution. As precipitation occured, the position of equilibrium shifted in the direction of the trans isomer. The ease with which isomerization occurs is illustrated by the work of Howell,[20a] in which <u>trans</u>-$W(CO)_4(PBu_3)_2$ isomerized to cis intramolecularly at 46 ^0C. In our work, dissolution of the trans isomer in $CDCl_3$ slowly leads to the formation of cis isomer. It is apparent that a a low energy barrier exists for the isomerization reaction.

The identification of the cis and trans isomers was established with both infrared spectra of the carbonyl stretching region and proton decoupled P-31 NMR spectra of the complexes. The trans isomer of D_{4h} symmetry shows one strong absorption (E_u), 1890 cm^{-1}, in the carbonyl region of the infrared spectrum (Figure 1). A weak

forbidden B mode (1946 cm^{-1}) also appears. The cis isomer (C_{2v}) gives rise to four active bands ($2A_1 + B_1 + B_2$) in the carbonyl region of the infrared spectra. The pure cis isomer was never obtained, but a mixture of cis and trans isomers (Figure 2) was commonly found. Overlap of three absorptions from the cis isomer with the E_u mode of the trans gives a broad absorption at about 1900 cm^{-1} and a strong cis absorption at 2020 cm^{-1}. Carbonyl stretching frequency data for various complexes are given in Table I.

A proton decoupled P-31 NMR spectrum of a trans/cis mixture (not at equilibrum) of $W(CO)_4(PPh_2CH=CH_2)_2$ is shown in Figure 3. The upfield signal centered at 12.3 ppm arises from the cis isomer while the signal at 18.7 ppm arises from the trans isomer. The satellites associated with each signal arise from the 14.28 % abundant W-183. Tungsten-phosphorous coupling constants of 231.5 Hz and 281.7 Hz were obtained for the cis and trans isomer respectively.

The <u>fac</u>-$W(CO)_3(PPh_2CH=CH_2)_3$ isomer was also identified with IR and NMR methods. The C_{3v} complex gives rise to A_1 and E modes which are IR active. The two strong absorption bands (Figure 4) at 1941 and 1842 cm^{-1} correspond to those absorption modes. The P-31 NMR (Figure 5) shows an absorption at 12.1 ppm with a tungsten-phosphorus coupling constant of 218.9 Hz.

The complex, <u>trans</u>-$W(CO)_4(\eta^1\text{-}PPh_2CH_2CH_2PPh_2)_2$, was

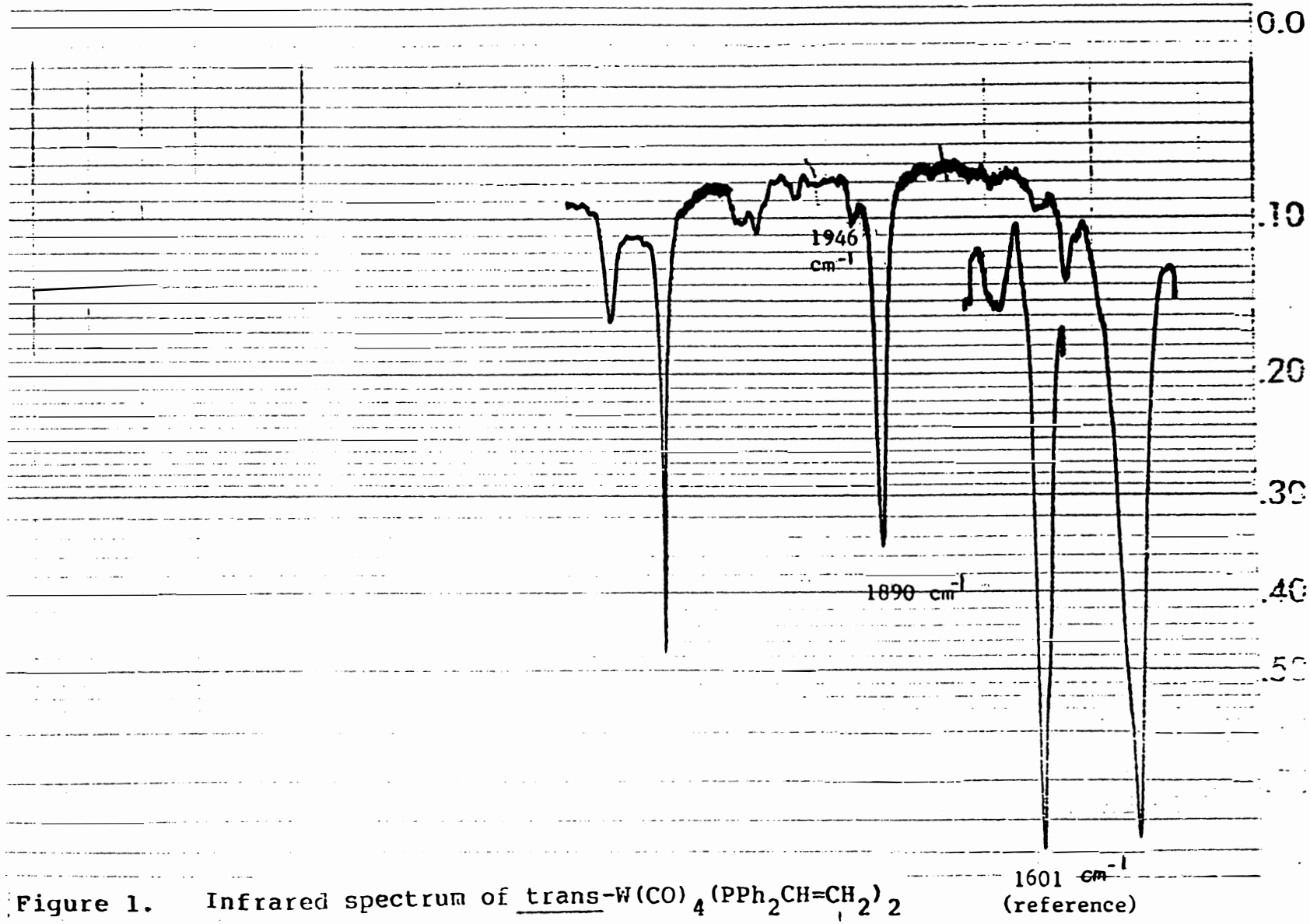
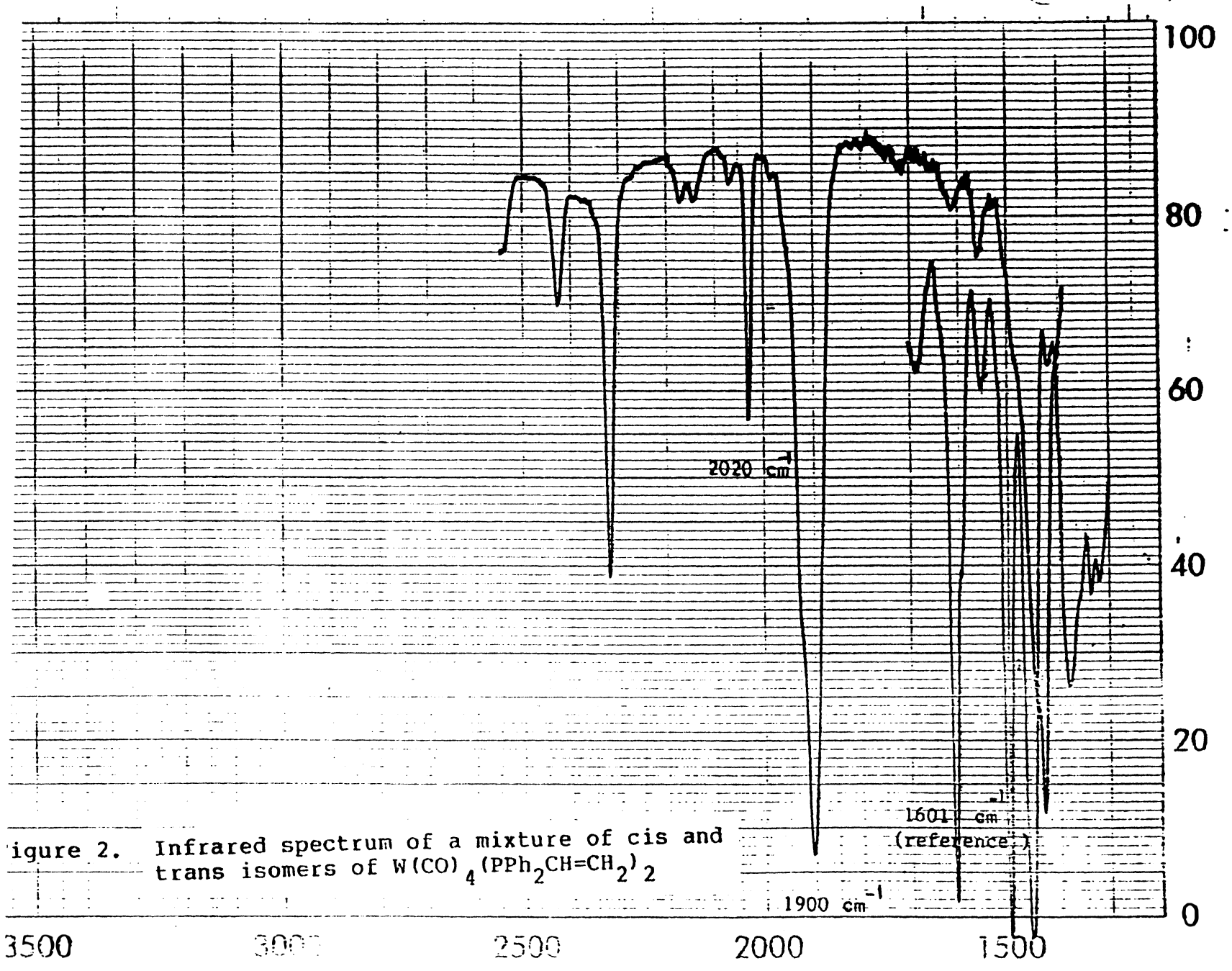
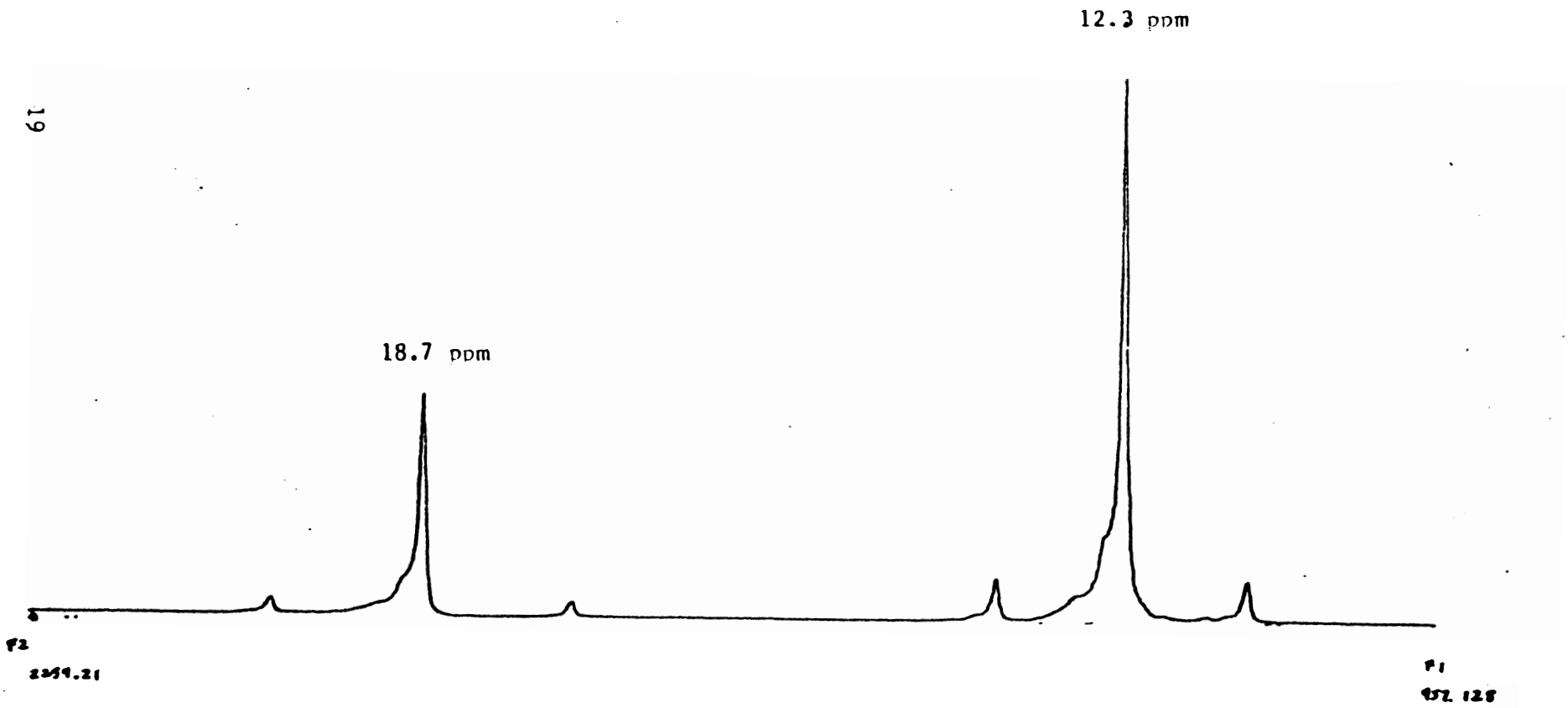


Figure 1. Infrared spectrum of trans-$W(CO)_4(PPh_2CH{=}CH_2)_2$



igure 2. Infrared spectrum of a mixture of cis and trans isomers of $W(CO)_4(PPh_2CH=CH_2)_2$

Figure 3. P-31 NMR spectrum of a mixture of cis and trans isomers of $W(CO)_4(PPh_2CH=CH_2)_2$



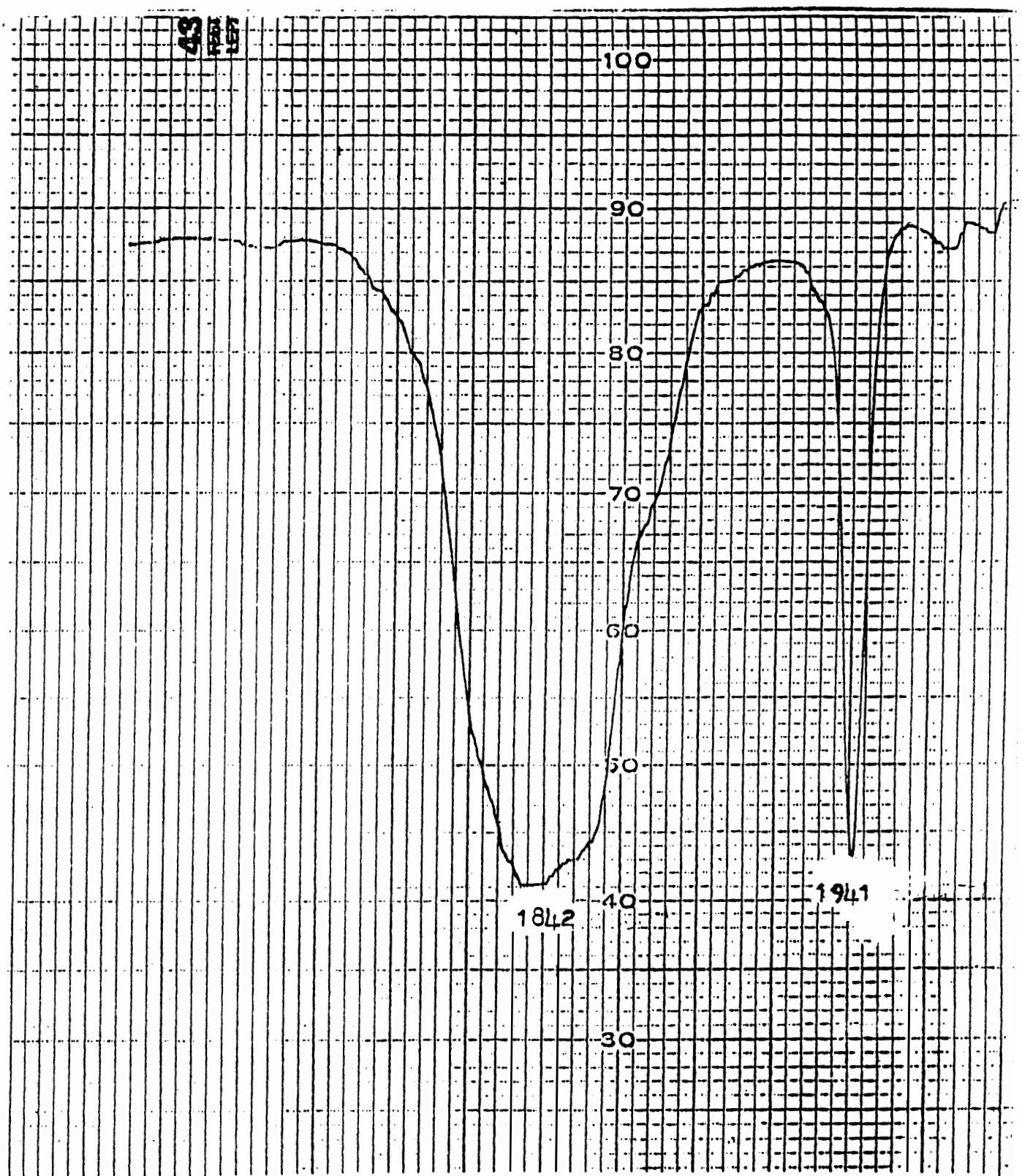
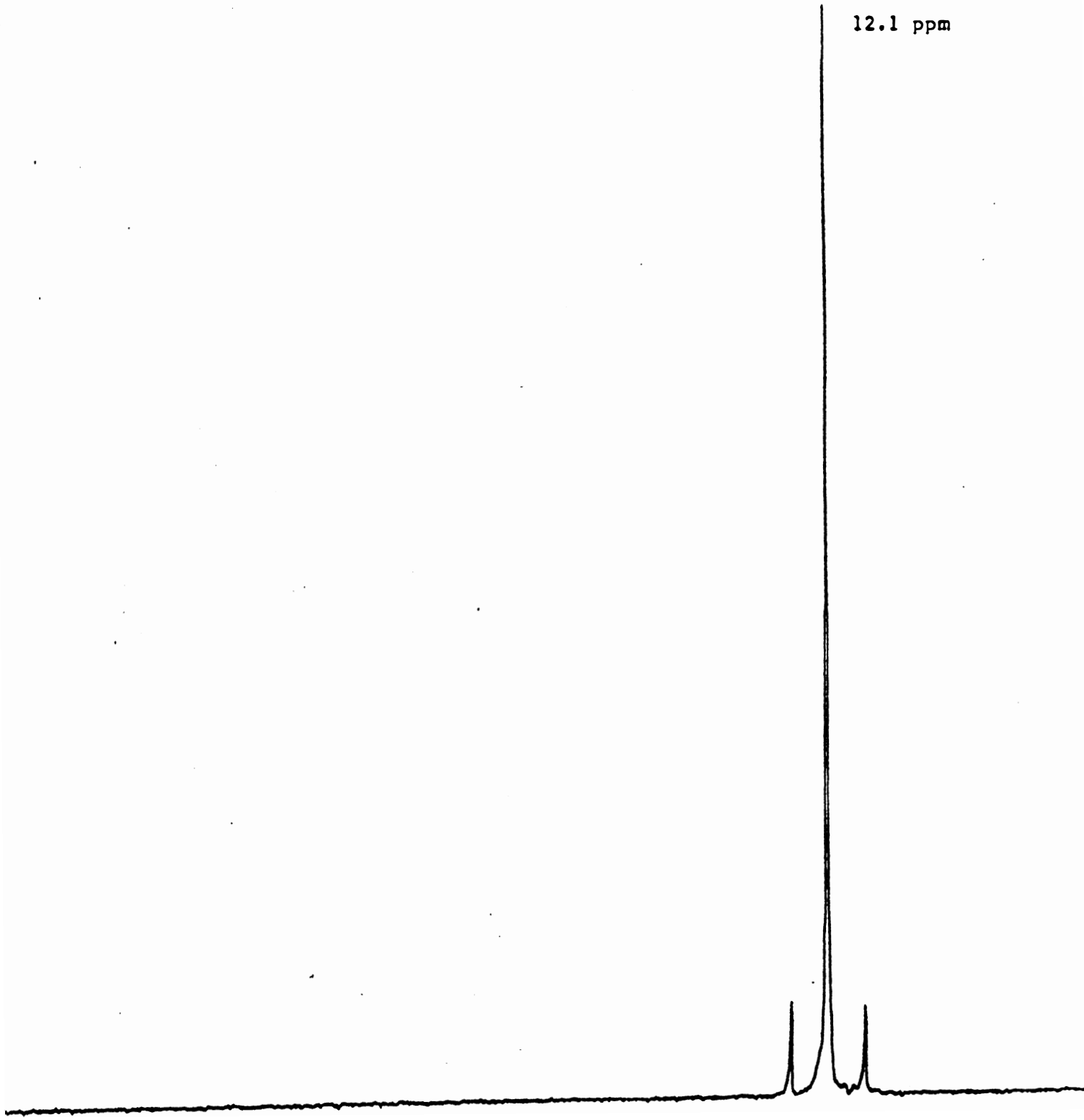


Figure 4. Infrared spectrum of fac-$W(CO)_3(PPh_2CH{=}CH_2)_3$

Figure 5.

P-31 NMR spectrum of fac-$W(CO)_3(PPh_2CH{=}CH_2)_3$

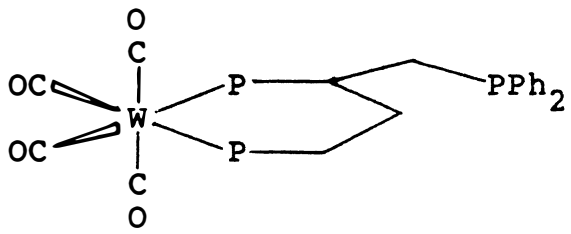


synthesized following the literature method:[14]

$$\underline{\text{trans}}\text{-}(OC)_4W(PPh_2CH{=}CH_2)_2 + 2PPh_2H \xrightarrow[60\ ^0C]{(CH_3)_3COK} \underline{\text{trans}}\text{-}(OC)_4(PPh_2CH_2CH_2PPh_2)_2$$

Good yields, consistent with those previously reported, were obtained. In most cases the starting material was contaminated with the cis isomer. Likewise the trans product was contaminated with the cis product. The P-31 spectrum of the product, although complex, clearly shows the coordination of two unidentate diphos molecules (Figure 6). The two principal sets of signals found at 18.8 ppm and -12.1 ppm are assigned to trans product. The AA'XX' spin sysytem gives rise to a doublet for both the A and X portions of the spectrum, corresponding to $\left|J_{ax} + J_{ax'}\right|$ which represents one-half of the total intensity. In addition there are two inner lines and two outer lines for each multiplet corresponding to the other half of the intensity. Analysis of NMR spectra of compounds of AA'XX' spin system have been disscussed in detail by Harris.[26] The separation between an outer line and the first inner line corresponds to $J_{aa'}$ ($^2J_{pp}$ = 54.3 Hz). The spectrum also shows the presence of <u>cis</u>-$W(CO)_4(PPh_2CH_2CH_2PPh_2)_2$, characterized by signals at 12.7 ppm and -12.2 ppm (overlapping with the trans isomer). For this complex $^2J_{pp}$ is 21.3 Hz. Both the cis and trans isomer show tungsten-phosphorus coupling. For the trans

isomer J_{wp} is 279 Hz while J_{wp} is 231.6 Hz for the cis isomer. It will noted that the spectrum contains three sets of signals in addition to those corresponding to the cis and trans isomers. These signals, centered at 17.7 ppm, 4.0 ppm and -20.1 ppm, correspond to a cyclic product, $(OC)_4W[PPh_2CH_2CH_2CH(PPh_2)CH_2PPh_2]$,

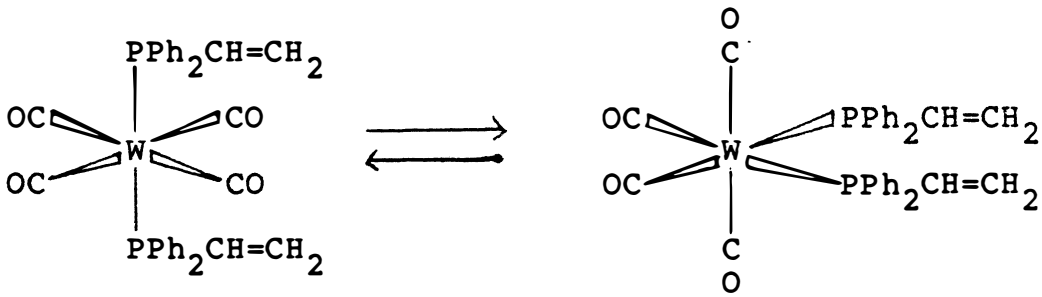


This compound was obtained previously by Sun from a free radical reaction[14] but this is the first time

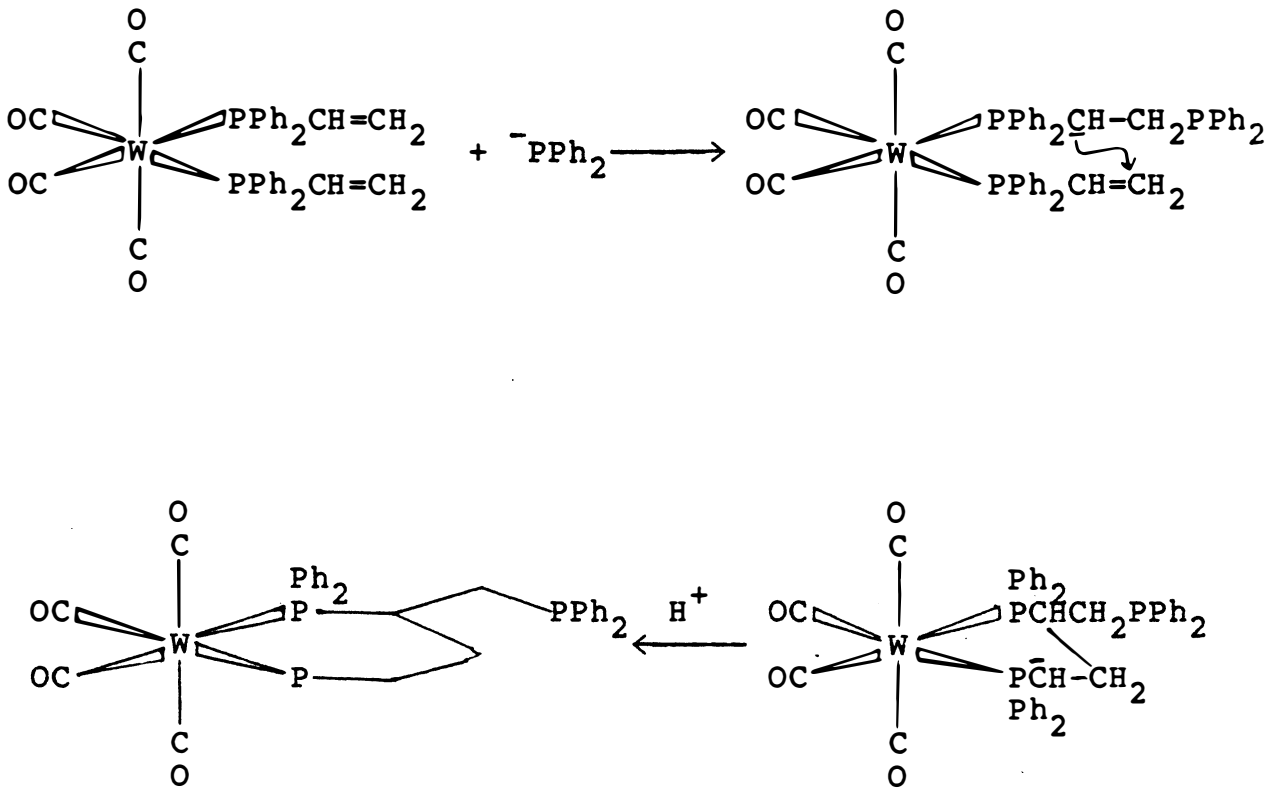
$$(OC)_4W(PPh_2CH{=}CH_2)_2 + PPh_2H \xrightarrow[\text{AIBN}]{} (OC)_4W(PCH_2CH_2CH(PPh_2)CH_2PPh_2)$$

$$\text{AIBN} = NC(CH_3)_2CN{=}NC(CH_3)_2CN$$

the product has been obtained by base promotion. The mechanism for the reaction is likely to be as follows:



$$PPh_2H + {}^{-}OBu^t \longrightarrow {}^{-}PPh_2 + HOBu^t$$



The P-31 NMR spectrum for <u>trans</u>-$W(CO)_4(\eta^1\text{-}PPh_2CH_2\text{-}CH_2PPh_2)_2$ was simulated with the aid of a computer (Figure 7a and 7b). For this AA'XX' spin system, $J_{xx'}$ is assumed to be zero. In our simulation, coupling constants of 54.3 Hz and 37.6 Hz were used for $^2J_{pp}$ and $^3J_{pp}$ respectively. All other phosphorus-phosphorus coupling constants were assumed to be zero. The computer code (Appendix A) for simulation was written in FORTRAN 77 computer language. It consists of three parts - one main program and two subroutine programs. The main program translates data from the two subroutine programs into proper graphics. One subroutine program (CHIPING) deals with the matrix representation of the Hamiltonium

Figure 6.

P-31 NMR spectrum of a mixture of cis and trans isomers of $W(CO)_4(PPh_2CH_2CH_2PPh_2)_2$ and a cyclic compound, $W(CO)_4(PPh_2CH_2CH_2CH(PPh_2)CH_2PPh_2$

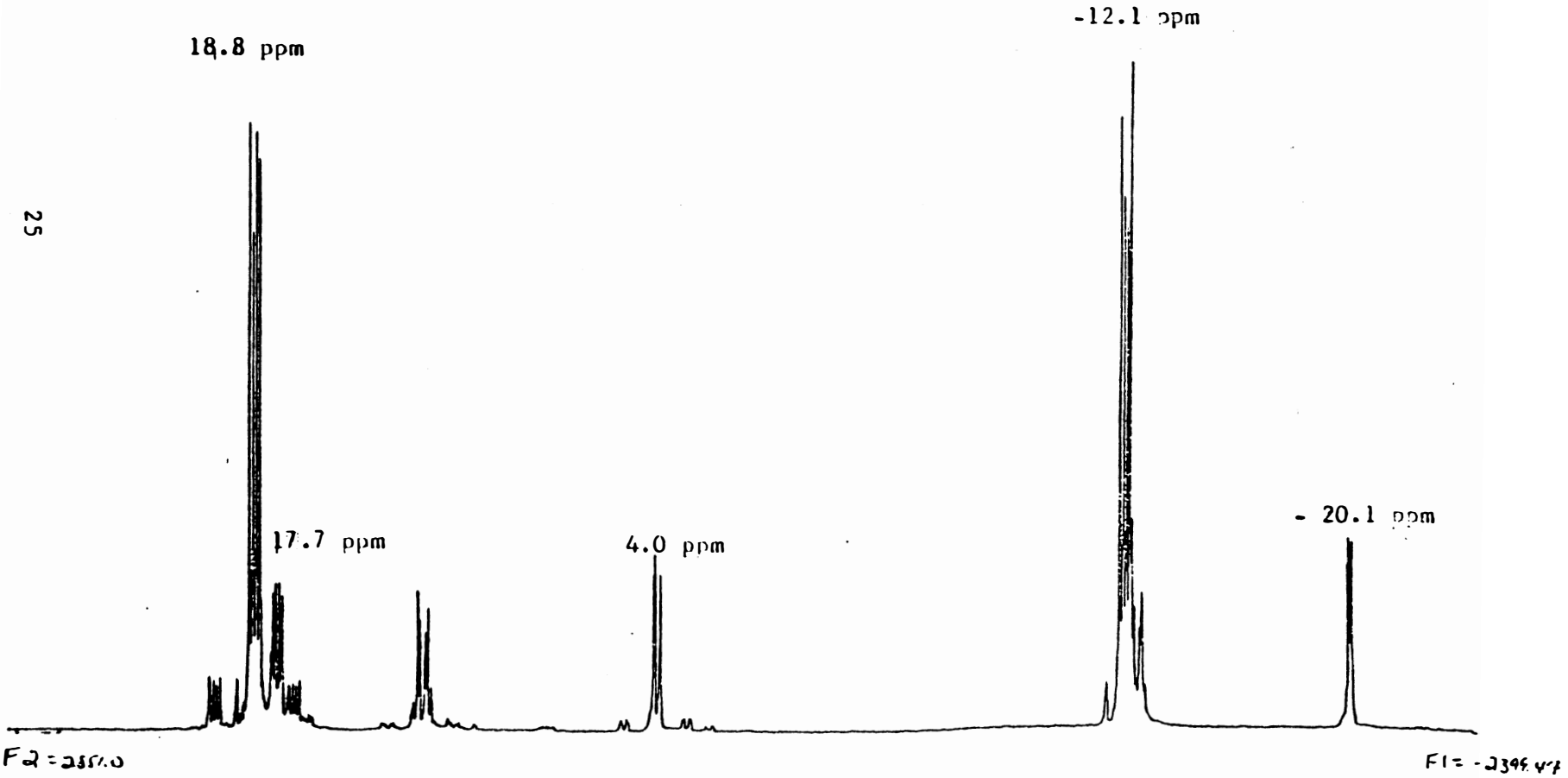


Figure 7

(a) Simulated P-31 NMR spectrum of trans-$W(CO)_4(\eta^1\text{-}PPh_2CH_2CH_2PPh_2)_2$

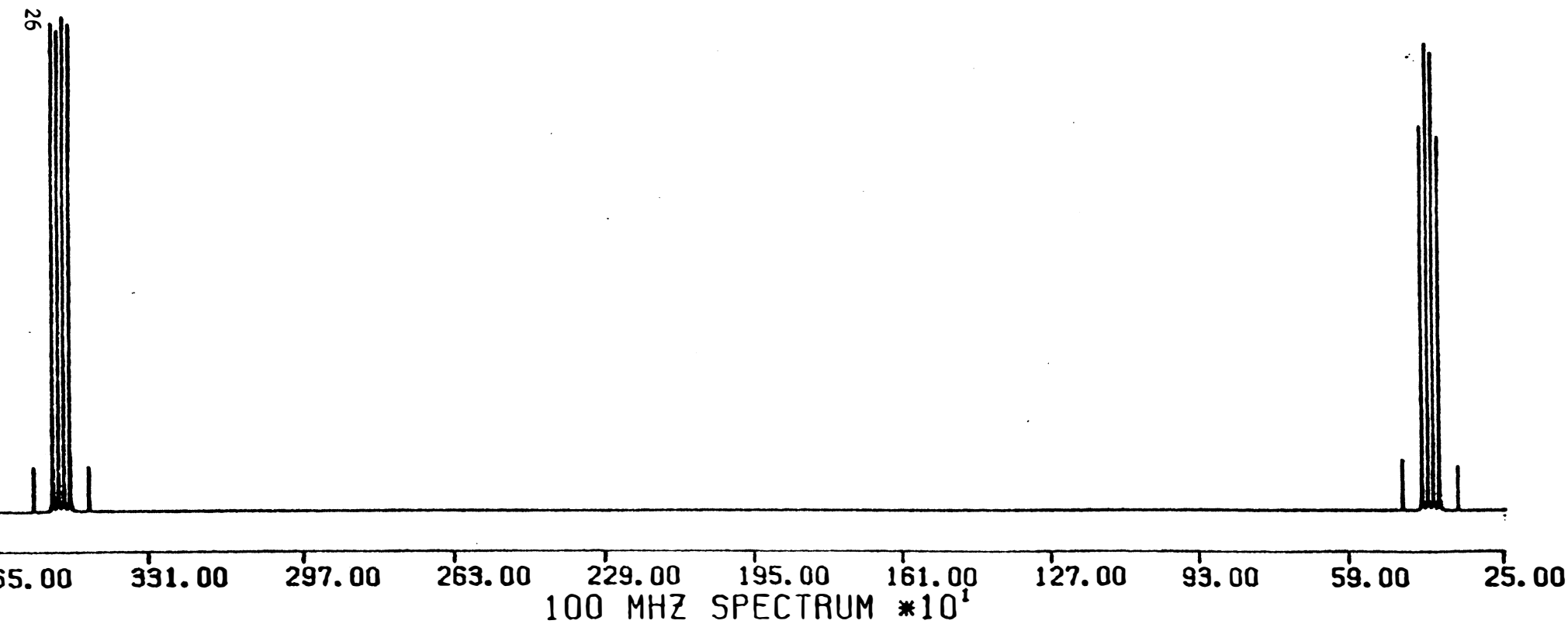
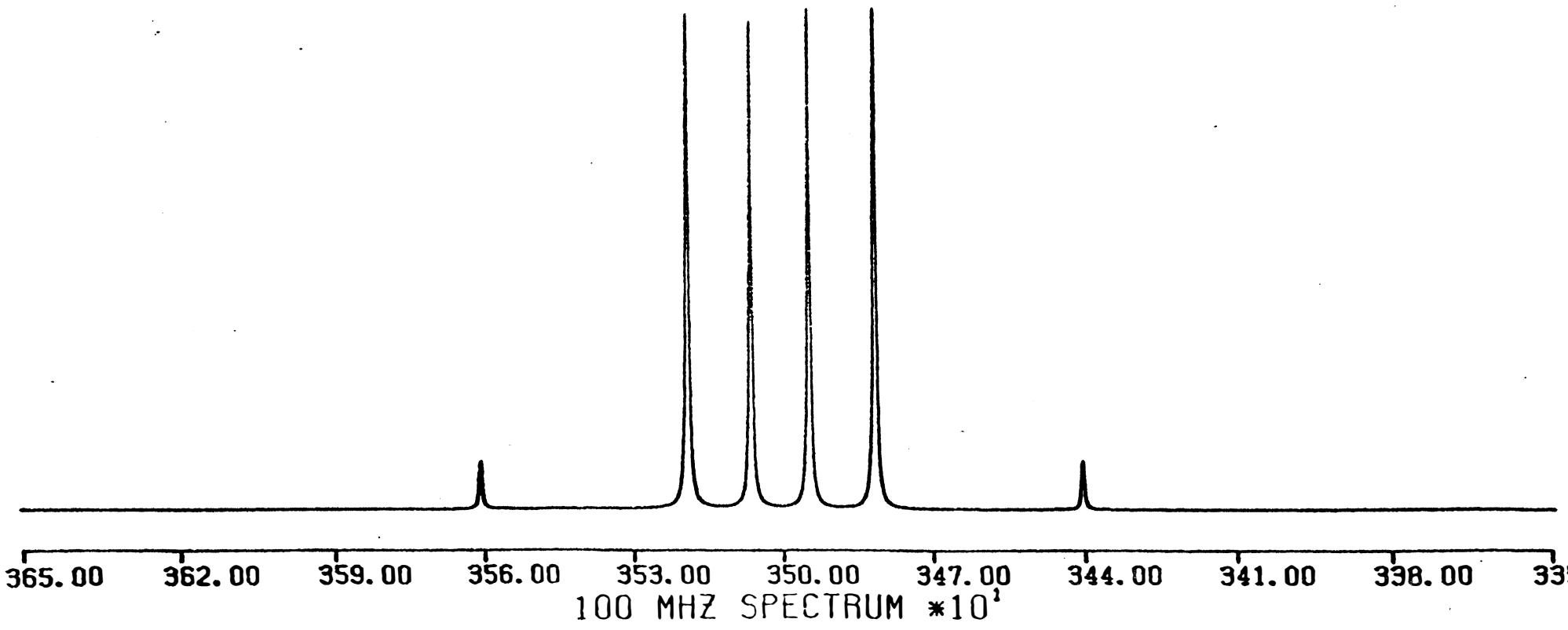


Figure 7

(b) Expanded simulated P-31 NMR sprctrum of trans-$W(CO)_4(\eta^1\text{-}PPh_2CH_2CH_2PPh_2)_2$.



and the calculation of the energies which are transition allowed as well as the relative intensities of each absorption peak. The other subroutine (HDIAG) diagonalizes the Hamiltonium matrix.

Before this code was used in practice, it was tested by three known compounds, 2,6-dimethoxyphenol, thiophene and 1,2-dichloro-3,4,5,6-tetrafluorobenzene. The excellent results (see appendix B) makes one feel quite confident in using this code for simulation. One more significant feature of this code is that it can be applied to any number of spin systems. The logic of this code was built for a general case, not for any specific spin system. One can apply this code to as large a spin system as one wants by simply increasing the value in the dimension statement properly.

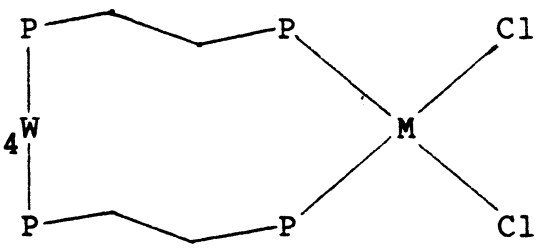
The following reaction sequence was used to prepare the tungsten-platinum and tungsten-palladium heterobimetallic complexes.

$$MCl_4^{=} + COD \longrightarrow MCl_2(COD) + 2\ Cl^-$$

COD = cyclooctadiene

$$\underline{trans}\text{-}W(CO)_4(\eta^1\text{-}PPh_2CH_2CH_2PPh_2)_2 + MCl_2(COD)$$

$$\xrightarrow[25\ ^0C]{CH_2Cl_2}$$



+ COD

M = Pd, Pt

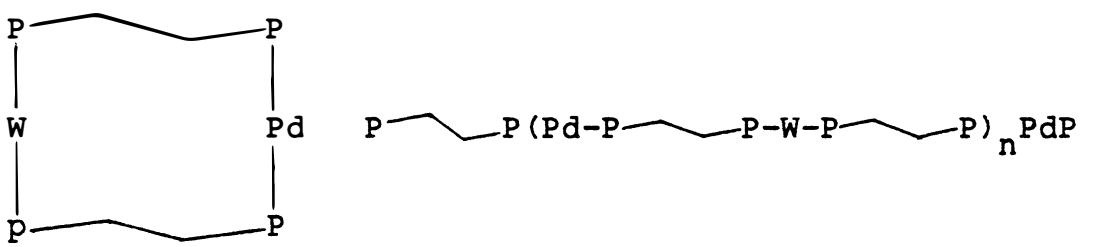
Direct reaction of the phosphine with $MCl_4^=$ was avoided since chelating ligands are known to give $[M(L\text{-}L)_2][MX_4]$ type complexes.

The reaction between the phosphine and $MCl_2(COD)$ was carried out under dilute conditions as described in the experimental section in an attempt to prevent polymerization. The products from these reactions were extremely insoluble. The tungsten-platinum complex was very pale yellow while the tungsten-palladium complex was yellow. Elemental analysis for the palladium and platinum products were less than satisfactory. The best result was for the tungsten-palladium complex (See experimental). The result for the tungsten-platinum complex was not convincing, nevertheless it appears likely that the predicted bimetallic complex is present and that purity is low because of the difficulty associated with the purification of the highly insoluble material. Both P-31 and IR spectra confirm that the complexes contain both tungsten and platinum or palladium centers. The complexes have been submitted to Johns Hopkins University for mass spectral analysis to determine the molecular weight of the species and thus the monomeric, dimeric or polymeric nature of the molecules. Unfortunately results have not been obtained after a three month wait.

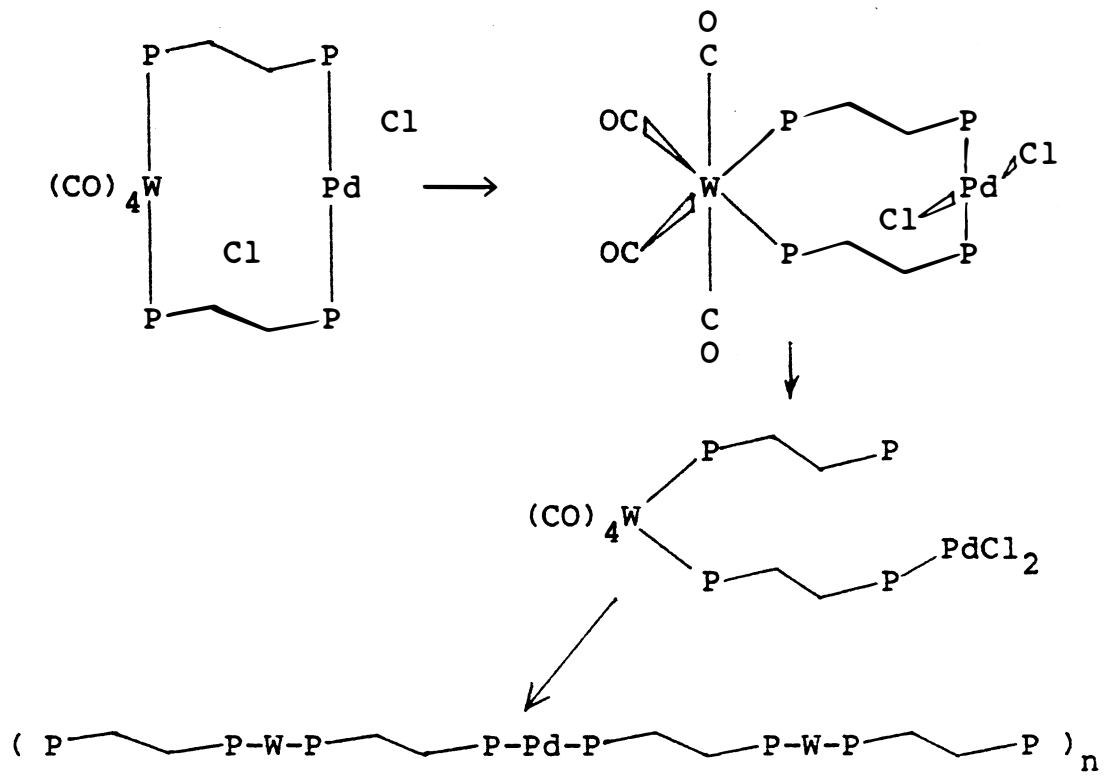
Both the palladium and platinum complexes showed slight solubility in CH_2Cl_2 and $CHCl_3$. The P-31 spectra are shown in Figures 8 and 9. The infrared spectra for

the carbonyl region are shown in Figures 10 and 11, while for the Pd-Cl and Pt-Cl region in Figures 12 and 13. The former IR spectra were obtained in CH_2Cl_2 while the latter were obtained as NUJOL mulls. Stretching frequencies are found in Table I and chemical shifts are given in Table II.

Very poorly resolved spectra were obtained for both the tungsten-platinum and tungsten-palladium complexes. The best result was obtained for the tungsten-palladium complex (Fig. 8). After 3967 accumulations, two broad principal signals were obtained at 20.3 ppm and 18.9 ppm. In addition a signal at 11.5 ppm was observed. The signal at 18.9 ppm is assigned to a phosphorus ligand occupying a trans position in tungsten tetracarbonyl. This is consistent with the value of 18.7 ppm found in the starting material, <u>trans</u>-$W(CO)_4(\eta^1\text{-}PPh_2CH_2CH_2PPh_2)_2$. The chemical shift at 20.3 ppm fits a trans arrangement of phosphorus ligands in palladium dichloride. The chemical shift for <u>trans</u>-$(Ph_2Et)_2PtCl_2$, which should be very similar to our complex, is reported to be 19.7 ppm.[27] Thus, based on P-31 NMR analysis, a trans-trans arrangement is possible whether or not the complex is a monomer or a polymer.



The signal at 11.5 ppm could correspond to cis geometry arround tungsten. If steric strain were present in the trans-trans complex, isomerization to a cis-trans arrangement would not be surprizing. The solution of the sample appeared colloidal after the sample run was completed. The broadness of the signals, the lack of resolution, and the inability of the investigator to observe tungsten-phosphorus satellites all point to polymer formation. It is well known that T_1 becomes longer as polymer length increases which in turns leads to a broad signal.[28] If polymer formation is important it is likely that a variety of molecular weights exist in the mixture. Slightly different chemical shifts of a variety of products could lead to broadened signals. Monomeric forms may be unstable with respect to polymerization. Thus, as time passes more and more polymer formation may occur. It is known that the trans isomer is more stable than the cis in square planar palladium phosphine complexes. If one examines the Van der Waals radii of the atoms in the monomeric tungsten-palladium complex it is apparent that some interaction may exist between the CO ligand of W and the Cl ligand of palladium. Thus there would be pressure for rearrangement to a cis or a polymeric structure. In addition, palladium complexes are known to be somewhat labile. Polymerization could occur when one end of a chelating phosphorus ligand becomes unhinged. The following sequence could be imagined:



The infrared spectrum of the carbonyl region (Fig 10) confirmed the trans arrangement about tungsten. A far infrared spectrum of the tungsten-palladium complex was obtained in an attempt to assign the Pd-Cl stretching frequency (Figure 12). Based on literature assignment,[29] the absorption at 337cm^{-1} can be assigned as the Pd-Cl stretch but other absorptions present in the region make the assignment inconclusive.

A glance at the P-31 NMR spectrum of the tungsten-platinum complex (Fig. 9) reveals two broad signals centered at 19.6 ppm and 7.3 ppm, obtained after 1059 accumulation. As for the tungsten-palladium complex, the signal at 19.6 ppm may be assigned to trans geometry which implied that there is no geometry change about tungsten when the

dangling phosphorous groups coordinate to platinum. The signal at 7.30 ppm is close to that published for cis-$(Ph_2Et)_2PtCl_2$ (9.8 ppm).[30] In general, trans phosphine complexes of platinum are difficult to obtain and our results are consistent with the prefered cis arrangement. The spectrum also shows platium-phosphorus satellites (J_{Pt-P}= 4414 Hz) arising from the 33 % abaundance Pt-195 isotope (I = 1/2). The tungsten-phosphous satellites were not resolved in this spectrum. It is known that platinum-phosphorus coupling constants are larger in cis complexes than in trans by about 2500 Hz.[31] Thus, P-31 NMR provides a convenient way to distinguish between cis and trans complexes. The value of 4414 Hz, although slightly larger than most cis complexes, is far too large to be a trans complex.

Our desire to obtain a P-31 spectrum in which fine structure was resolved led us to obtain computer plots based on an estimation of coupling constants in the tungsten-platinum compound (Figure 14). As with the starting material, the spin system should be AA'XX', but in this case $J_{xx'}$ is unequal to zero. A value of 500 Hz was used in the computer code, based on typical phosphorus-phosphorus coupling constants in known square planar complexes.[28] Poor resolution in our experimental spectra prevents the drawing of significant conclusion regarding the correctness of our assignment.

The IR and far-IR spectra of the tungsten-platinum

complex are shown in Figures 11 and 13 respectively. The trans stereochemical arrangement around tungsten was confirmed by the carbonyl IR spectrum. In the far-IR region three absorptions were present, which could be assigned to Pt-Cl stretching modes. A cis arrangement for a square planar platinum complex has local C_{2v} symmetry and should give rise to two IR active modes (A_1 and B_2) while a trans geometry, prossesing local D_{2h} symmetry should have only one IR active Pt-Cl stretch. The two absorptions, 295 and 318 cm^{-1} fall into the region reported in the literature[29] for cis complexes and the absorption at 339 cm^{-1} is consistent with a trans arrangement.[32] Since the P-31 NMR spectrum did not show a signal for a trans platinum complex we conclude that either the absorption does not arise from a Pt-Cl stretch or that the solid state IR spectrum reveals a geometry that is not present in the solution P-31 spectrum. This could occur if the trans-trans isomer was significently less soluble than the trans-cis isomer or if the trans isomer isomerized to cis in solution.

The insolubility of the bimetallic products and the broadness of the P-31 absorption arising from these complexes led us to strongly suspect that the direct method of mixing <u>trans</u>-$W(CO)_4(\eta^1\text{-}Ph_2CH_2CH_2PPh_2)_2$ and $(COD)MCl_2$ leads to polymerization. As an approach to the problem we explored briefly a method to reduce the probability of polymerization. In this approach both PPh_2H and PPh_2-

Figure 8.

P-31 NMR spectrum of $W(CO)_4(PPh_2CH_2CH_2PPh_2)_2PdCl_2$

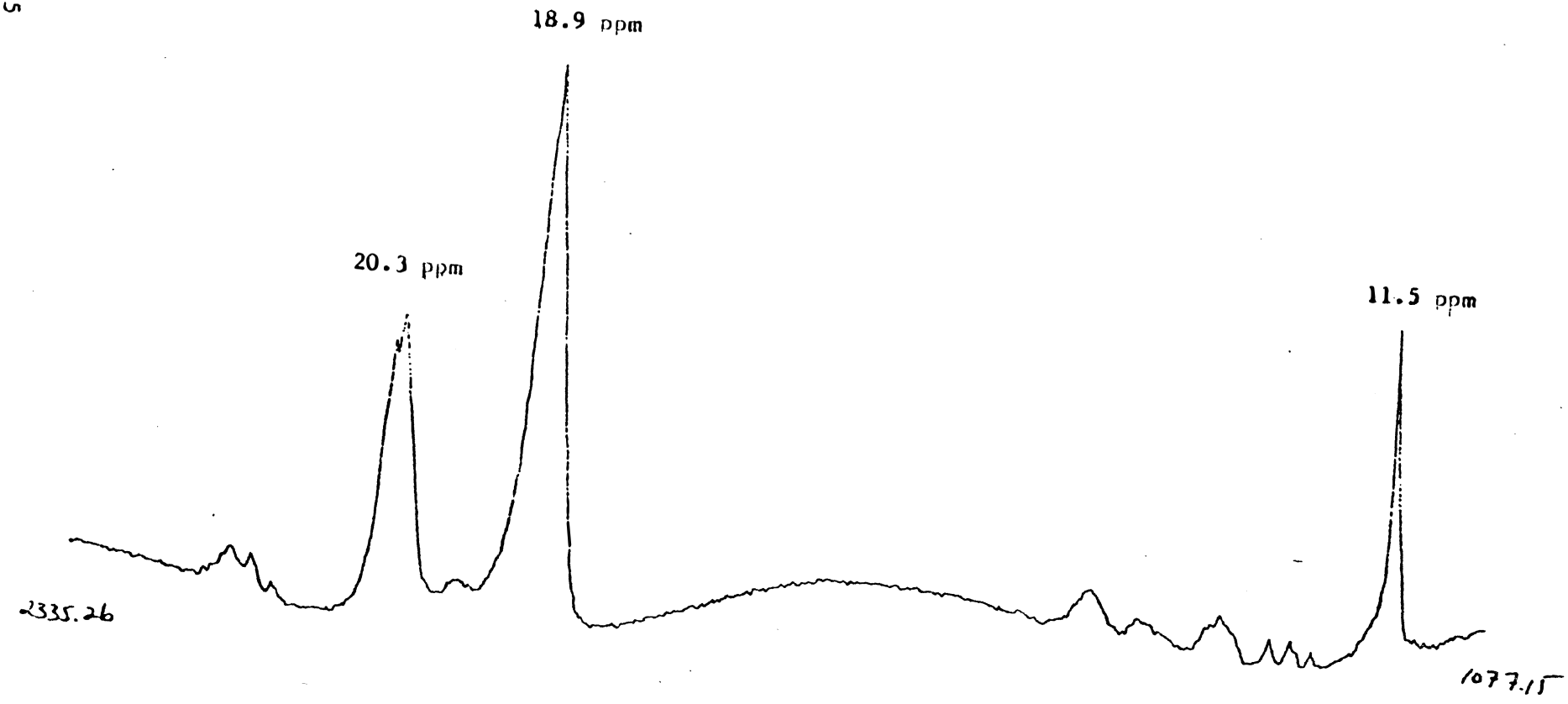


Figure 9. P-31 NMR spectrum of $W(CO)_4(PPh_2CH_2CH_2PPh_2)_2PtCl_2$

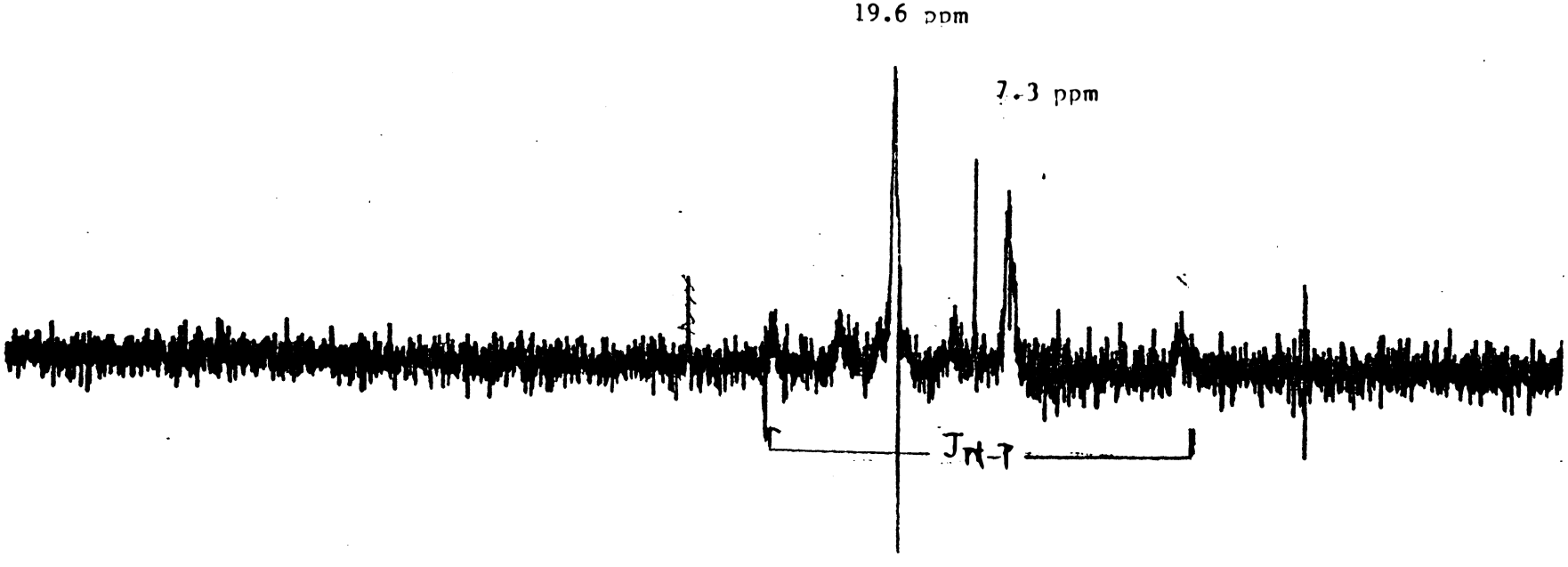
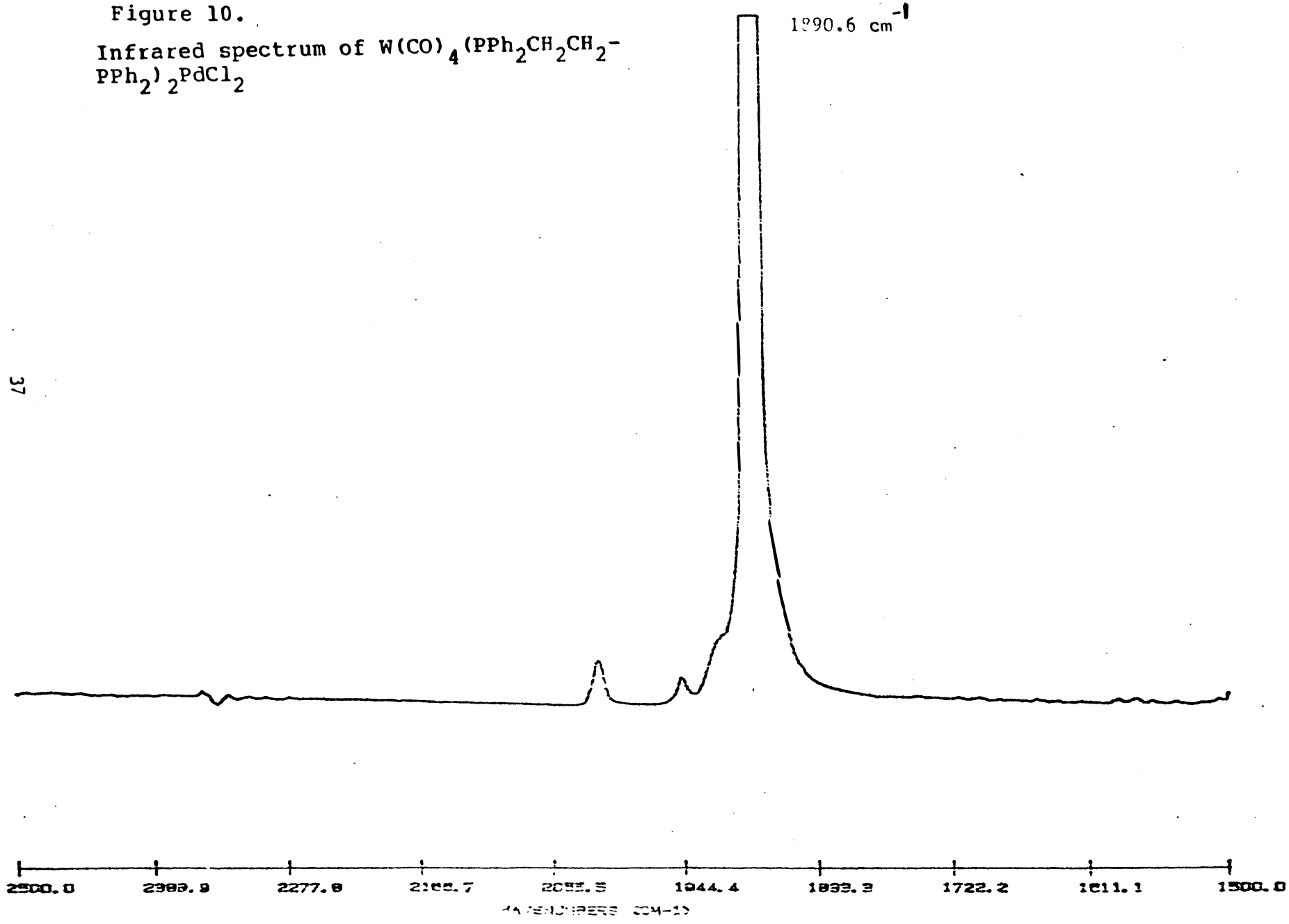


Figure 10.

Infrared spectrum of $W(CO)_4(PPh_2CH_2CH_2PPh_2)_2PdCl_2$



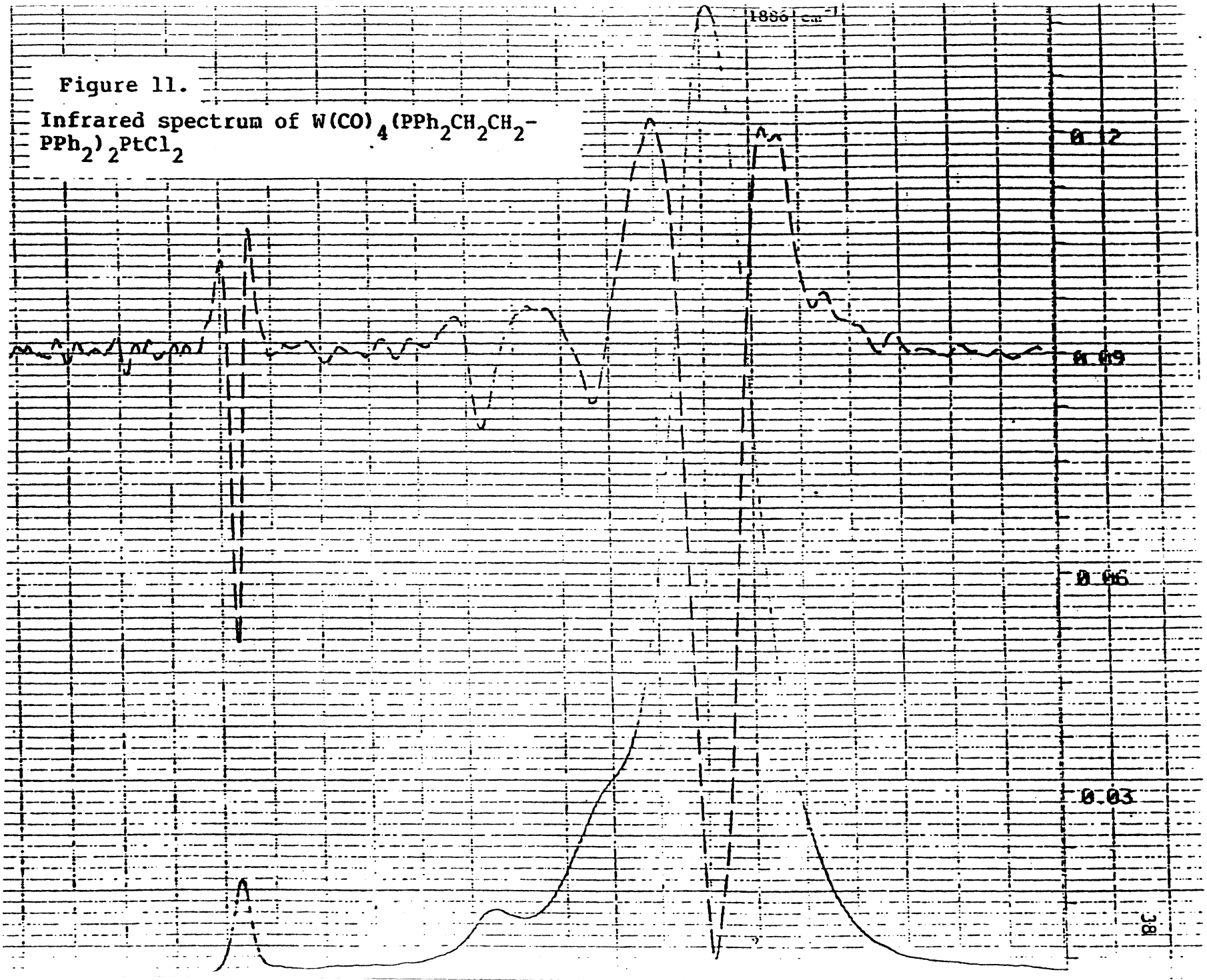


Figure 11.

Infrared spectrum of $W(CO)_4(PPh_2CH_2CH_2PPh_2)_2PtCl_2$

Figure 12.

Far-infrared spectrum of $W(CO)_4(PPh_2CH_2CH_2PPh_2)_2PdCl_2$

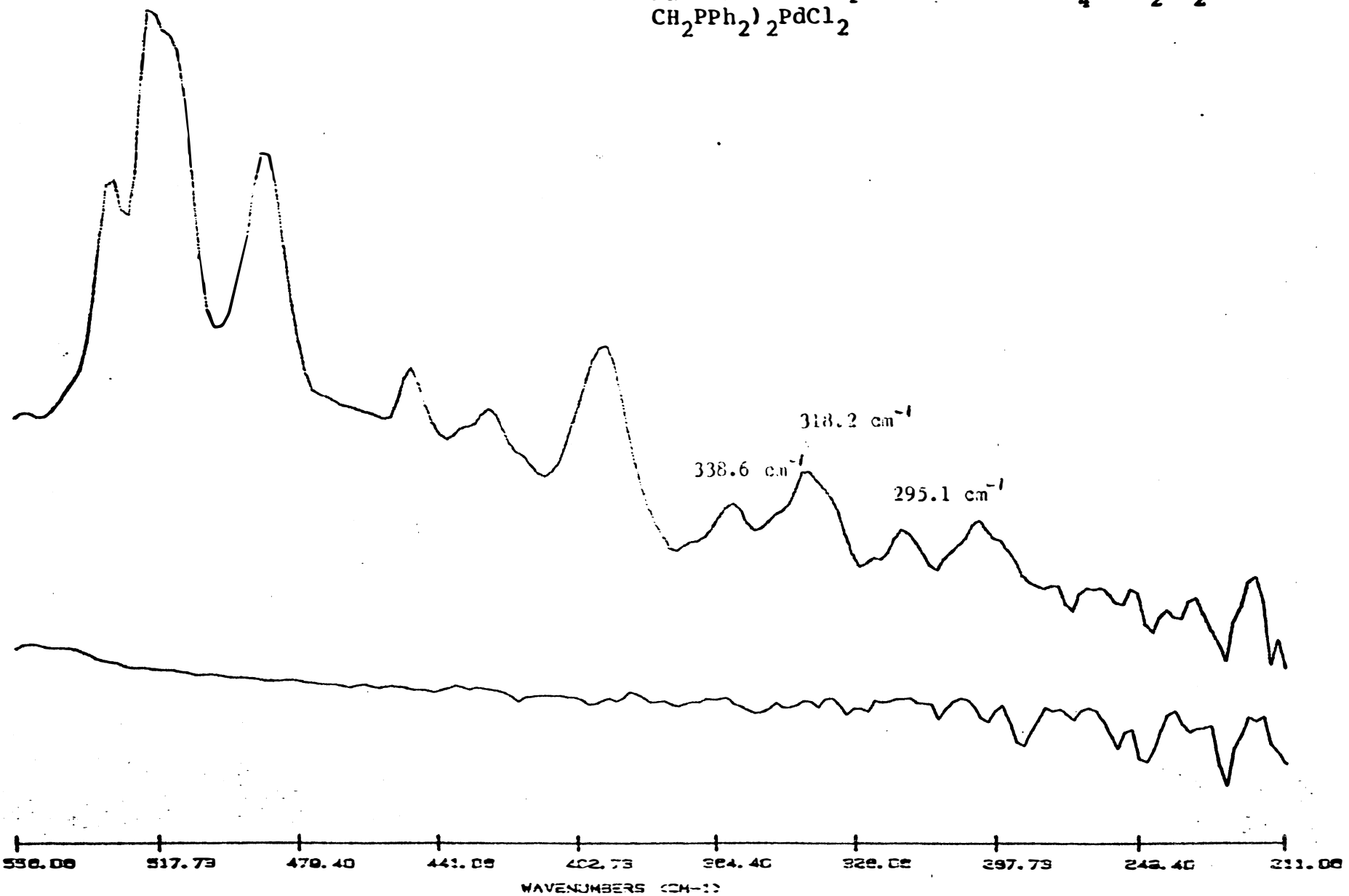


Figure 13.

Far-infrared spectrum of $W(CO)_4(PPh_2CH_2CH_2PPh_2)_2PtCl_2$

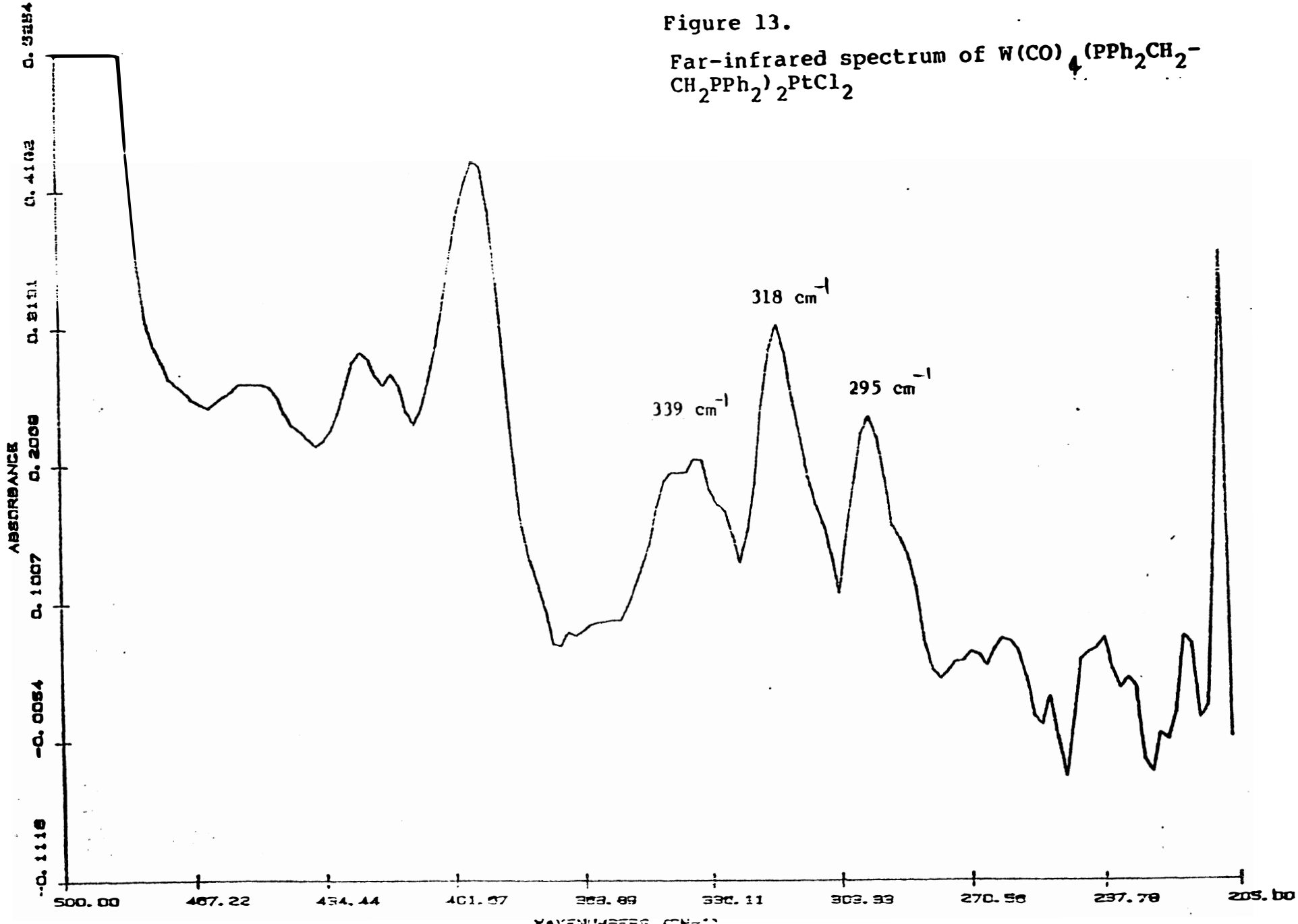
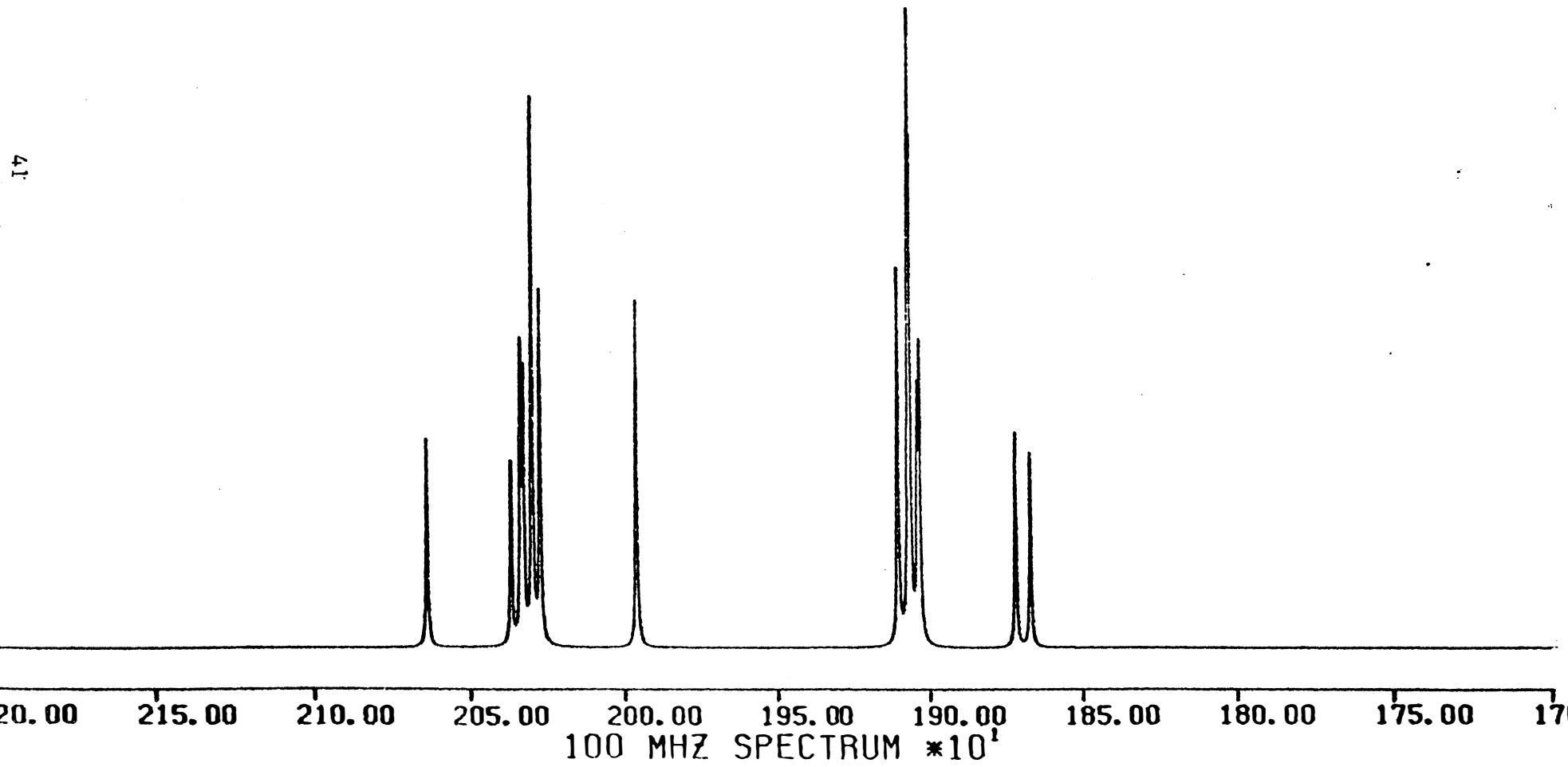


Figure 14.

Simulated P-31 NMR spectrum of $W(CO)_4(PPh_2CH_2CH_2PPh_2)_2PtCl_2$



$CH=CH_2$ were bound to metals and addition across the double bond was attempted.

$$(CO)_4W(PPh_2CH=CH_2)_2 + (Ph_2PH)_2MCl_2 \xrightarrow[THF]{(CH_3)_3COK} (OC)_4W(PPh_2CH_2CH_2PPh_2)_2MCl_2$$

OR

$$(CO)_4W(PPh_2H)_2 + (Ph_2PCH=CH_2)_2MCl_2 \xrightarrow[THF]{(CH_3)_3COK} (CO)_4W(\eta^1\text{-}Ph_2PCH_2CH_2PPh_2)MCl_2$$

The four starting materials were prepared as follows:

$$(COD)PdCl_2 + 2\ PPh_2CH=CH_2 \longrightarrow (Ph_2PCH=CH_2)_2PdCl_2$$

$$(COD)PdCl_2 + 2\ PPh_2H \longrightarrow (Ph_2PH)_2PdCl_2$$

$$K_2PtCl_4 + 2\ PPh_2CH=CH_2 \longrightarrow (Ph_2PCH=CH_2)_2PtCl_2 + 2\ Cl^-$$

$$K_2PtCl_4 + 2\ Ph_2PH \longrightarrow (PPh_2PH)_2PtCl_2 + 2\ Cl^-$$

Only one reaction with these starting materials was attempted and the result were so unpromising that the approach was not continued. These reactions should be explored more extensively in future work. The reaction which was carried out was as follows:

$$(OC)_4W(PPh_2CH=CH_2)_2 + (Ph_2PH)_2PtCl_2 \longrightarrow\ ?$$

A P-31 spectrum of the crude product is shown in Figure 15. Signals at 18.7 ppm and 18.9 ppm undoubtedly belong to a trans phosphine tungsten complex but no signals could

clearly be assigned to a platinum phosphorus species. Many other signals appeared in the spectrum. The signal at 41.5 ppm is consistent with a chelated $W(CO)_4(PPh_2CH_2CH_2PPh_2)_2$ complex.[29] It is apparent that the reaction is complex and does not appear promising.

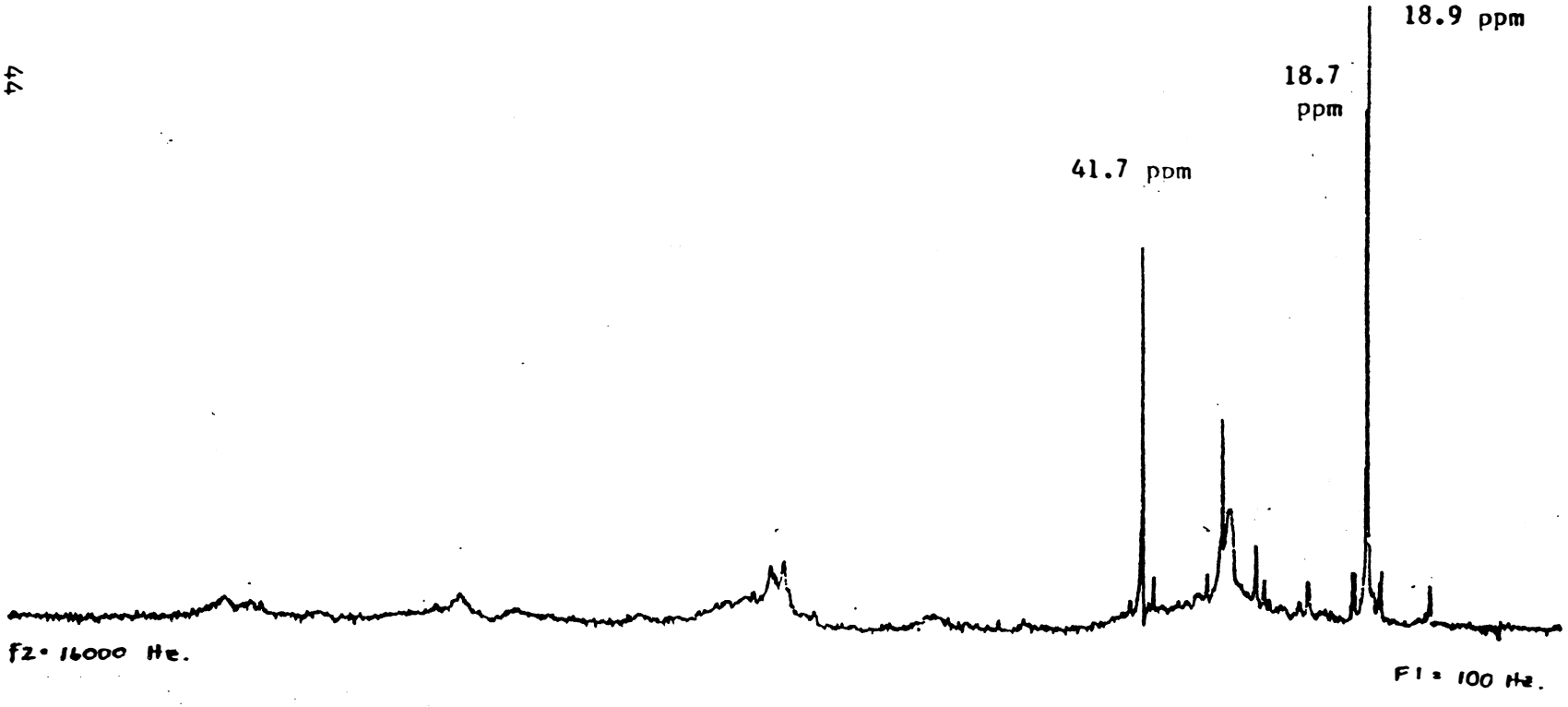
A surprising result was obtained when we attempted to prepare $W(CO)_4(PPh_2H)_2$ from $W(CO)_6$ and PPh_2H in the presence of $NaBH_4$. The disubstituted product was expected based on the results we had obtained with $PPh_2CH=CH_2$ which were described early in this thesis.

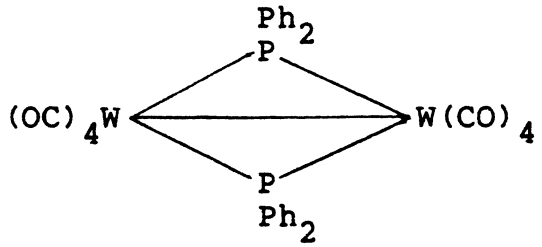
$$W(CO)_6 + 2\ Ph_2PH \xrightarrow[\text{n-butanol or ethanol}]{NaBH_4} (CO)_4W(PPh_2H)_2$$

After heating the reaction under reflux for six hours, a red product precipitated from the reaction mixture. The infrared spectrum of the carbonyl region of the red product was very complex (Figure 16) and no structure was postulated from its appearence. Thin layer chromatography revealed the presence of three distinct compounds. The P-31 NMR spectrum (Figure 17) of the crude product enabled us to identify two of the three compounds. The strong absorption at 181 ppm with tungsten-phosphorus satellites (J_{wp} = 164 Hz), was assigned to $W_2(CO)_8(PPh_2)_2$ based on literature reports.[5] The structure is shown on page 45. The absorptions at 177, 156 and -13 ppm arise from $W_2(CO)_7(PPh_2)_2(PPh_2H)$. This compound

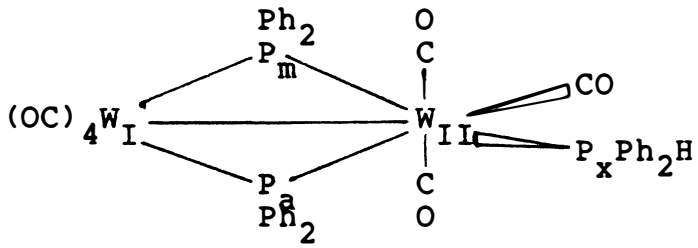
Figure 15.

P-31 NMR spectrum of the reaction, $W(CO)_4$-$(PPh_2CH=CH_2)_2$ + $(Ph_2PH)_2PtCl_2$, crude product.





was reported previously by P. M. Treichel but no structure assignment was made.[33] Based on the coupling pattern present in the spectrum we propose the following structure:



The two phosphido bridge are nonequivalent giving rise to the absorptions at 177 and 156 ppm. The phosphido bridge which is trans to two CO groups probably gives rise to the absorption at 177 ppm. Other compounds in the literature which have phosphido bridges are $W_2(CO)_7(COMe)(PPh_2)_2$ (167 ppm), $W_2(CO)_7(COBu)(PPh_2)_2$ (167 ppm), and $W_2(CO)_7(MeCOMe)(PPh_2)_2$ (174 ppm).[34] The absorption at -13 ppm may be assigned to the terminal secondary phosphine. A careful examination of the expanded spectra of the absorptions at 177 and 156 ppm (Figure 18a, 18b) show each of them to be a doublet of doublets with more than forteen tungsten-phosphorus satellites in each set. The proposed structure of $W_2(CO)_7(PPh_2)_2PPh_2H$ contains two magnetically nonequivalent tungsten atoms. Therefore

each tungsten will couple differently to each phosphorus and that gives rise to four tungsten-phosphorus coupling constants for the phosphido bridges. If no overlap of satellite lines occured, one would expect to see two sets of eight absorptions. The signal at -13 ppm (Fig. 19c) at first glance appears to be a triplet but close inspection shows it to be a doublet of doublets with the two inner lines overlapping with one another. The following coupling constants were extracted from the spectra.

$$J_{am} = 16.4 \text{ Hz}$$
$$J_{ax} = 34.4 \text{ Hz}$$
$$J_{mx} = 32.8 \text{ Hz}$$
$$J_{w(I)-p(a)} = 160.2 \text{ Hz}$$
$$J_{w(II)-p(a)} = 191.4 \text{ Hz}$$
$$J_{w(I)-p(m)} = 150.1 \text{ Hz}$$
$$J_{w(II)-p(m)} = 184.1 \text{ Hz}$$
$$J_{w(II)-p(x)} = 245.3 \text{ Hz}$$

The mechanism for the $NaBH_4$ reaction undoubtedly involves abstraction of H^+ from Ph_2PH with the evolution of H_2. The Ph_2P^- anion is an active nucleophile and has two lone pairs on phosphorus which can bridge two metals.

In the course of synthesizing <u>trans</u>-$W(CO)_4(PPh_2CH{=}CH_2)_2$ in the $NaBH_4$ reaction, it was discovered that if excess $PPh_2CH{=}CH_2$ were used a high yield of <u>fac</u>-$W(CO)_3(PPh_2CH{=}CH_2)_3$ could be obtained.

$$W(CO)_6 + \text{excess } Ph_2PH \longrightarrow \underline{fac}\text{-}(OC)_3(PPh_2CH{=}CH_2)_3 + 3\ CO$$

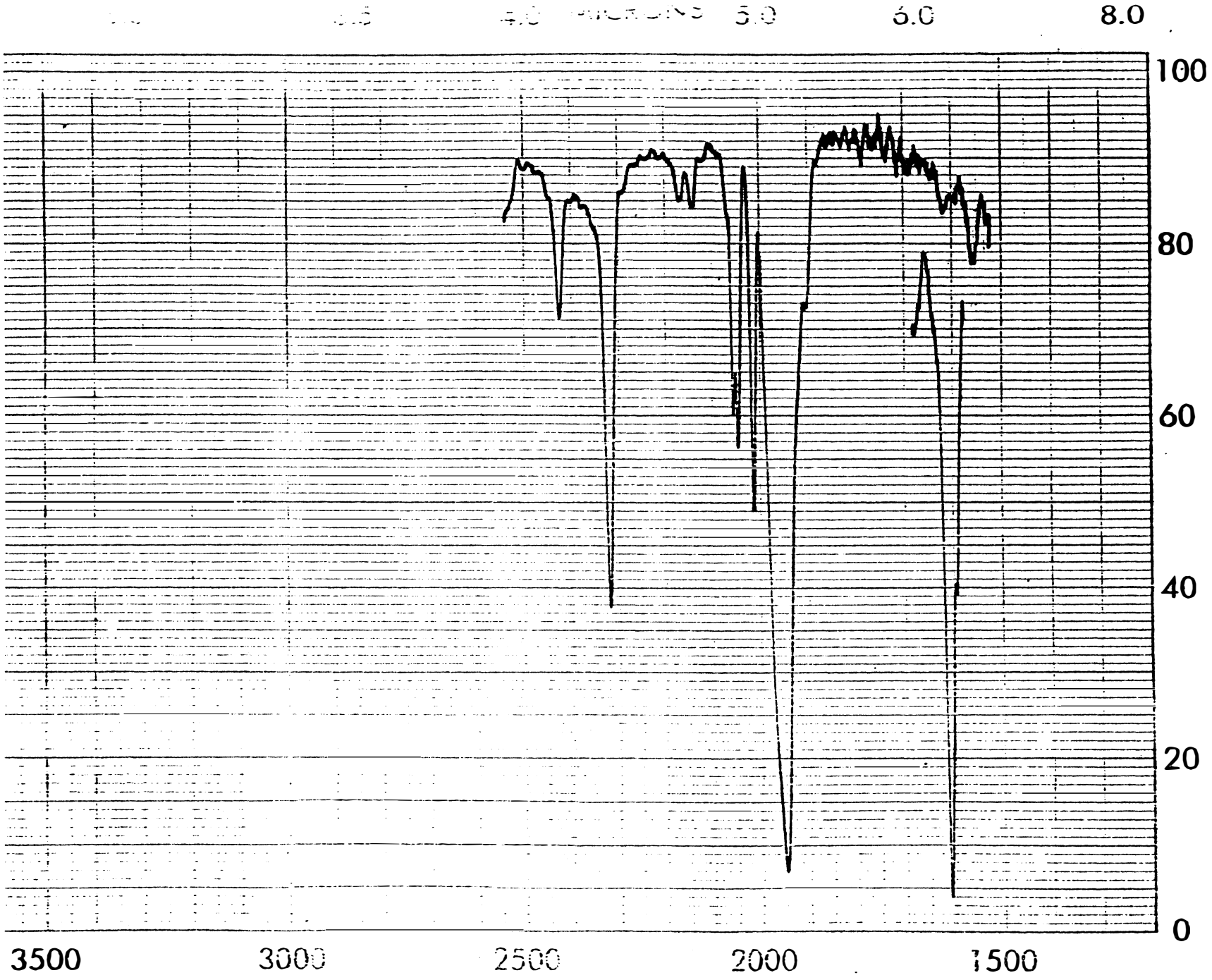


Figure 16. Infrared spectrum of the reaction, $W(CO)_6$ + 2 Ph PH + NaBH crude product

Figure 17.

P-31 NMR spectrum of the reaction, $W(CO)_6$ + 2 Ph_2PH + $NaBH_4$, crude product

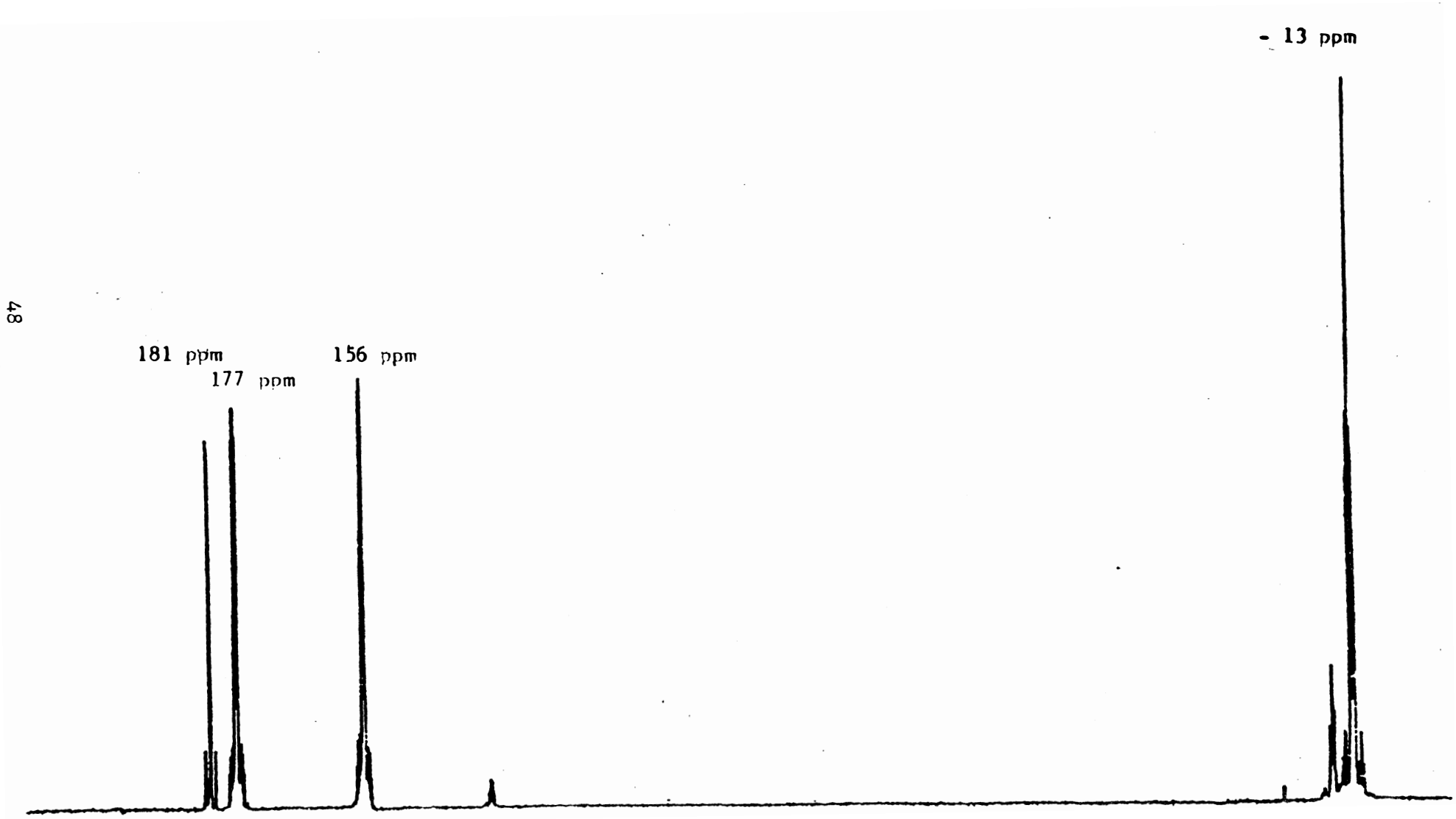


Figure 18

(a) Expanded P-31 NMR spectrum (177 ppm region of Fig. 17)

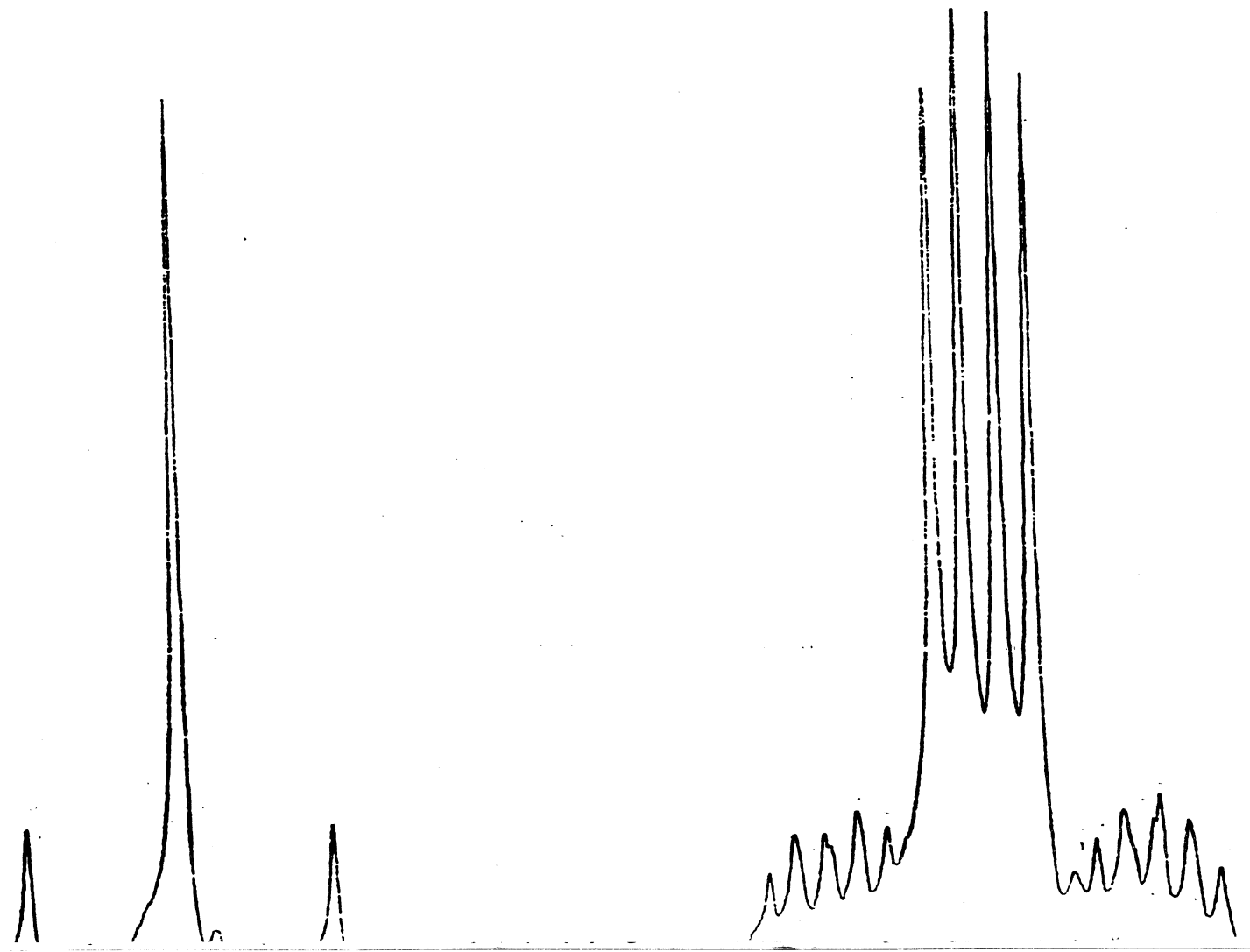


Figure 18

(b) Expanded P-31 NMR spectrum (156 ppm region of Fig. 17)

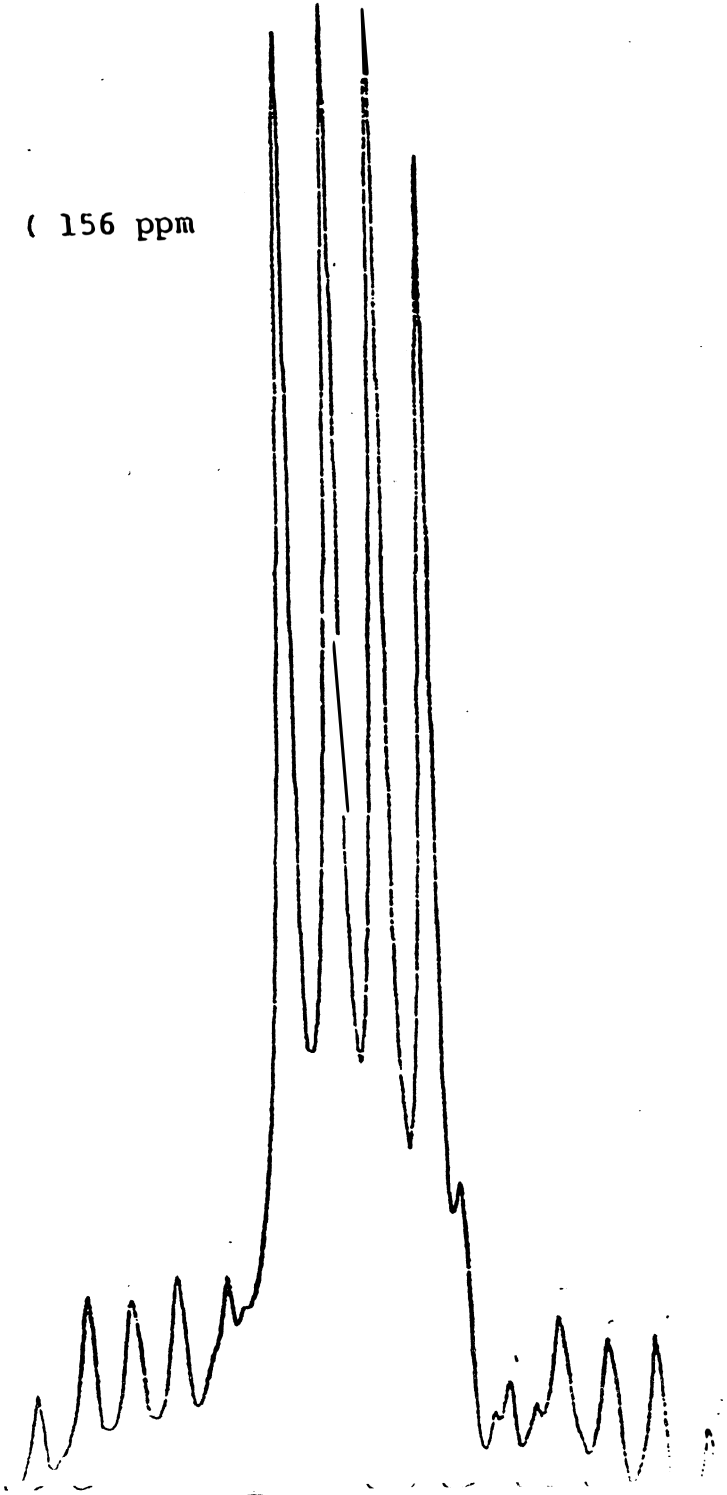
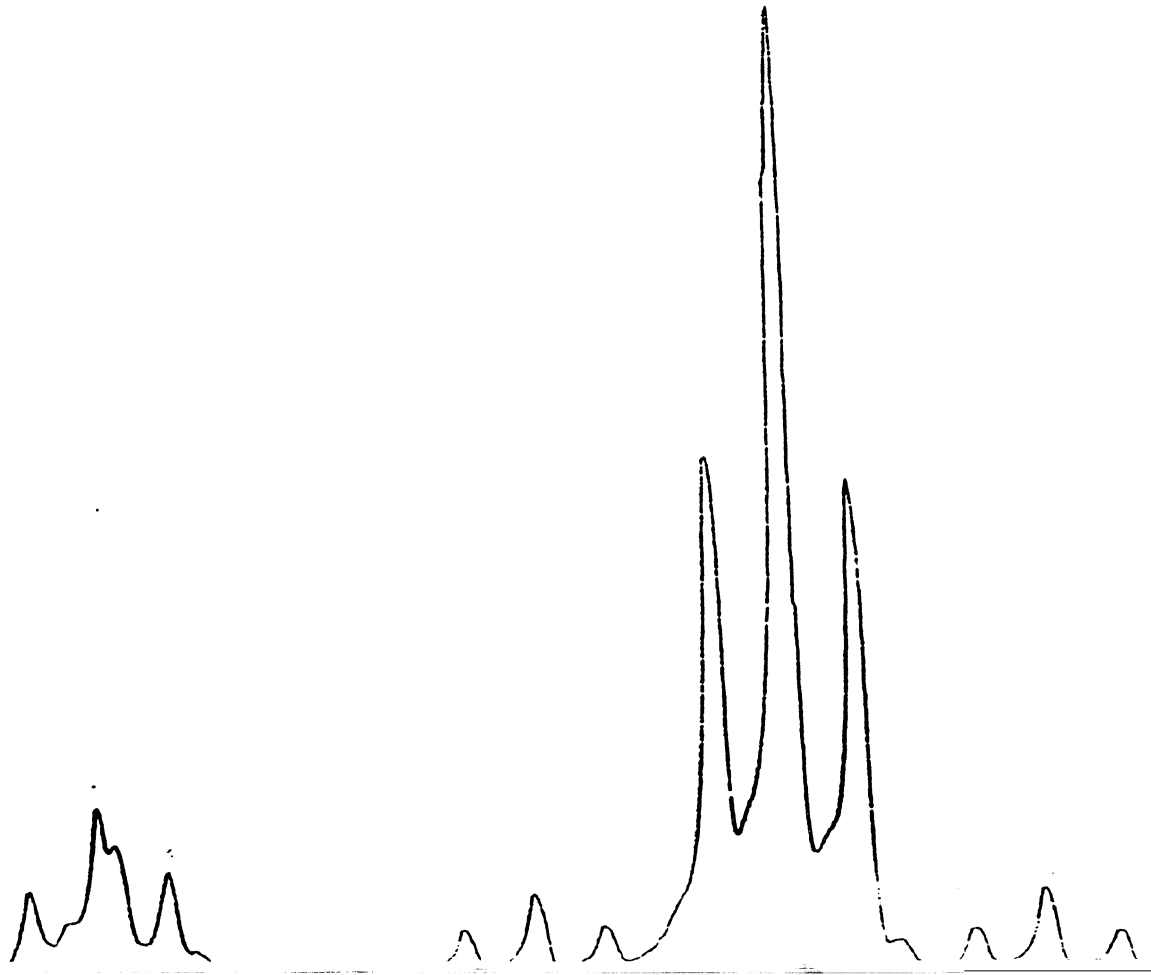


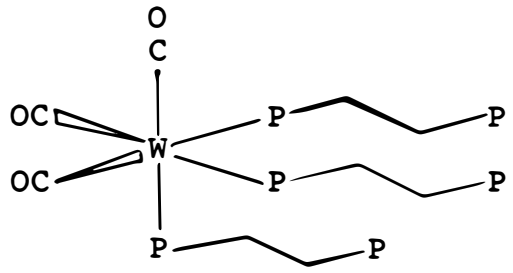
Figure 18

(c) Expanded P-31 NMR spectrum (-13 ppm region of Fig. 17)

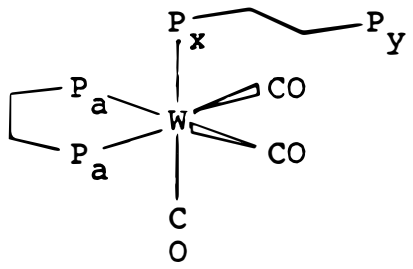


A project was undertaken to utilize the facial product to prepare the first tris unidentate ditertiary phosphine,

$$\underline{fac}\text{-}(CO)_3W(PPh_2CH{=}CH_2)_3 + 3\ Ph_2PH \xrightarrow{\text{base}}$$



In previous work in our research group, Hansen had carried out this reaction and obtained <u>fac</u>-$W(CO)_3$(diphos)(PPh_2H) which was identified with P-31 NMR.[35] The tris unidentate complex was not produced in the current work and neither was the Hansen work duplicated. In our reaction the principal product, based on the P-31 NMR spectrum, was <u>fac</u>-$W(CO)_3(\eta^2\text{-}PPh_2CH_2CH_2PPh_2)(\eta^1\text{-}Ph_2PCH_2CH_2PPh_2)$



Three principle absorptions were found in the P-31 spectrum (Figure 19). The intense doublet (J_{PaPx} = 22 Hz) at 35 ppm probably arises from chelated diphos.

Chemical shifts of chelated diphos are always much further downfield than nonchelated phosphines.[31] The absorption could also be assigned to a phosphine oxide but the small phosphorus-phosphorus coupling constant rules against such an assignment. The doublet (J_{PxPy} = 33 Hz) at -11 ppm corresponds nicely to a dangling diphos ligand. The central absorption at 9.1 ppm consists of a doublet of triplets with coupling constants consistent with those observed for the other two principal absorptions. This spectrum was computer simulated by method described earlier (Figure 20). The spectrum also reveals a less intense doublet (J_{pp} = 20 Hz) at 37 ppm which belongs to chelated diphos and could result from the presence of <u>fac</u>-$W(CO)_3$(diphos)($Ph_2PCH{=}CH_2$). The small absorptions at 17,18 and -20 ppm may arise from the cyclic compound, $W(CO)_4[PPh_2CH_2CH_2CH_2(CH_2PPh_2)PPh_2]$ discussed on page 23.

Several aspects of the work herein described need further investigation. There is no doubt but what we have synthesized complexes containing two different metals which are bridged by diphos. The molecular weights of these compounds have yet to be established. In the future, the compounds should be examined for catalytic activity. In addition, bimetallic complexes of tungsten and rhodium or iridium should be prepared as those are likely to show greater catalytic activity.

The reaction of $W(CO)_6$ with PPh_2H in the presence

Figure 19.

P-31 NMR spectrum of the reaction, fac-$W(CO)_3(PPh_2CH=CH_2)_3$ + 3 Ph_2PH, crude product

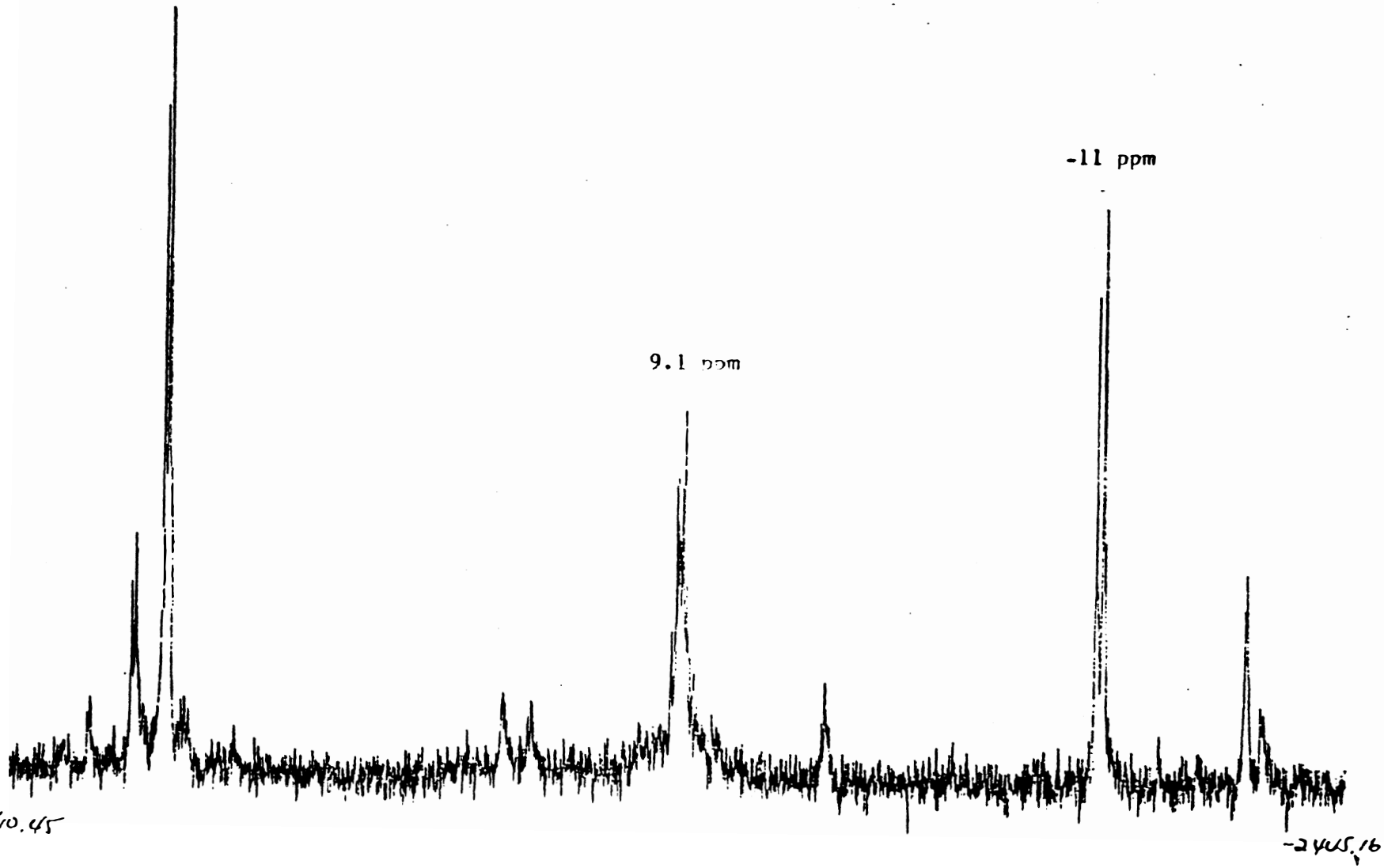
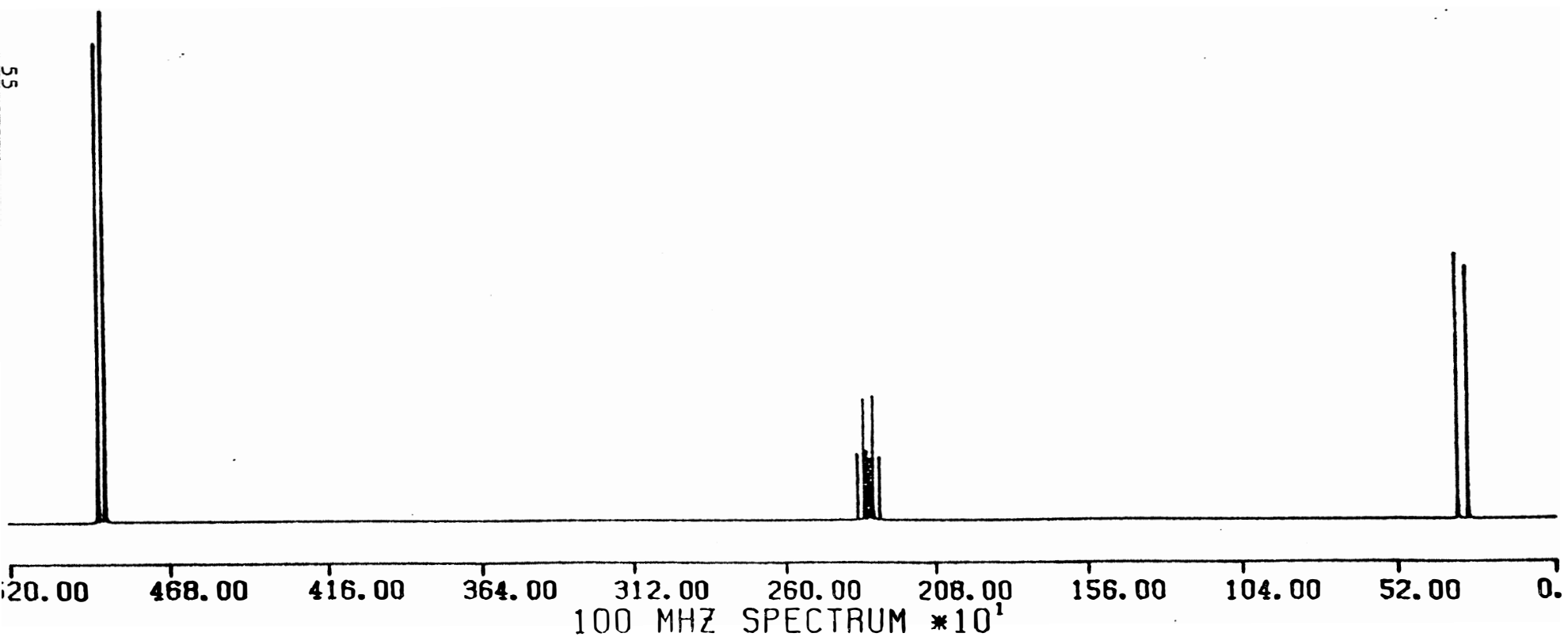


Figure 20.

Simulated P-31 NMR spectrum of *fac*-$W(CO)_3(\eta^1\text{-}PPh_2CH_2CH_2PPh_2)(\eta^2\text{-}PPh_2CH_2CH_2PPh_2)$



of $NaBH_4$ should be examined in detail as it could represent a general method of introducing phosphido bridges into a variety of tungsten complexes. It is possible that under certain condition highly substituted phosphido derivatives might be obtained.

Table II Phosphorus-31 nmr data of the tungsten carbonyl complexes

Compound	δ ppm coord	δ ppm uncoord	J_{pmp} Hz	J_{mp} Hz	J_{pp} Hz
cis-$W(CO)_4(PPh_2CH{=}CH_2)_2$	12.3	231.5			
trans-$W(CO)_4(PPh_2CH{=}CH_2)_2$	18.7		281.7		
fac-$W(CO)_3(PPh_2CH{=}CH_2)_3$	12.1			218.9	
trans-$W(CO)_4(PPh_2CH_2CH_2PPh_2)_2$	18.8	-12.1	54.3	279.0	
cis-$W(CO)_4(PPh_2CH_2CH_2PPh_2)_2$	12.7	-12.2	21.3	231.6	
$W(CO)_4(PPh_2CH_2CH_2CH(PPh_2)CH_2PPh_2)$	17.7	-20.1			
	4.0				
$W_2(CO)_8(PPh_2)_2$	181	164			
$W_2(CO)_7(PPh_2)_2(PPh_2H)$	177 (Pa)			160 (J1a)	16.4 (Jam)
	156 (Pm)			191.2(J11a)	34.4 (Jax)
	-13 (Px)			150.1(J1m)	32.8 (Jmx)
				184.1(J11m)	
				245.3(J11x)	
fac-$W(CO)_3(n^2\text{-}PPh_2CH_2CH_2PPh_2)$ $(n^1\text{-}PPh_2CH_2CH_2PPh_2)$	35 (Pa)				22 (Jax)
	-11 (Py)				33 (Jxy)
	9.1 (Px)				
$W(CO)_4(PPh_2CH_2CH_2PPh_2)_2PdCl_2$	18.9 (W)				
	20.3 (Pd)				
$W(CO)_4(PPh_2CH_2CH_2PPh_2)_2PtCl_2$	19.6 (w)			4414	
	-13 (Px)				

tetrachloroplatinum were purchased from Pressure Chemical Company.

Commercial n-butanol was used without further purification. THF and diglyme were dried over anhydrous $MgSO_4$ for two days. The solvent was filtered and further dried with sodium metal. Benzophenone was used as a a drying indicator. The solvent was heated under reflux until it turned blue, at which time it was disttilled into an oven dried receiver.

B. Preparation of Monometallic Complexes

(1) Preparation of <u>trans</u>-tetracarbonylbis(diphenylvinylphosphine)tugsten, <u>trans</u>-$W(CO)_4(PPh_2CH=CH_2)_2$

a. The $NaBH_4$ Reaction

Tungsten hexacarbonyl (5.3 g, 0.015 mole) was introduced into a 200 mL round-bottom flask. A Teflon coated magnetic stirring pea was added, followed by 100 mL of n-butyl alcohol. The flask was immersed halfway in an oil bath equipped with a heating coil. A magnetic stirring unit was placed under the oil bath. A thermometer also immersed in the oil bath, indicated the bath temperature. Nitrogen gas was bubbled into the solution through a glass inlet tube for approximately 10 minutes. During this period, diphenylvinylphosphine, $Ph_2PCH=CH_2$, (4.0 mL, 0.03 mole) was injected directly into the flask by means of a syringe. Sodium borohydride (0.8 g, 0.022 mole) was added to the flask and a condenser with a connecting stopcock was attached immediately after the

nitrogen inlet tube was removed from the solution.

Under a nitrogen atmosphere the reaction was carried out by heating the solution under reflux at 120 ^{0}C for six hours. The solution was cooled to room temperature and stood for two days. The solution was filtered and crude product was collected. Unreacted tungsten hexacabonyl in the crude product was removed by continuous vacuum sublimation at 50 ^{0}C for five hours.

The residue was washed twice with petroleum ether. The crude product was then recrystallized from dichloromethane-methanol to produce 3.43 g (32 % yield) of the desired complex. (M.P. 146-148 ^{0}C)

In an attempt to increase the yield, the refluxing time was increased to nine hours but the percentage yield did not increase. Also, the reaction was carried out with excess diphenylvinylphosphine under the same conditions, without an increase in yield.

b. The Diglyme Reaction

(1) Preparation of <u>trans</u>-tetracarbonylbis(diphenylvinylphosphine)tungsten, <u>trans</u>-$W(CO)_4(PPh_2CH{=}CH_2)_2$

The preparation of <u>trans</u>-$W(CO)_4(PPh_2CH{=}CH_2)_2$ was carried out following the published method.[14] The average yield based on five reactions was 29 %. The product was usually contaminated with the cis isomer as shown by IR spectra.

(2) Preparation of trans-tetracarbonylbis(tetraphenyldiphosphinoethane)tungsten(0), <u>trans</u>-$W(CO)_4(PPh_2CH_2$-

$CH_2PPh_2)_2$

The preparation of trans-$W(CO)_4(PPh_2CH_2CH_2PPh_2)_2$ was carried out following the published method.[14] In addition to the trans isomer of $W(CO)_4(PPh_2CH_2CH_2PPh_2)_2$ a cyclic compound, $W(CO)_4(PPh_2CH_2CH_2CH(PPh_2)CH_2PPh_2)$, was found in the crude product. After recrystallization from dichloromethane-methanol a yellow product (1.3 g; 31 %) was obtained (M.P. 150-152 ^0C).

(3) Preparation of cis-tetracarbonylbis(diphenylphosphine)tungsten, cis-$W(CO)_4(PPh_2H)_2$

The preparation of cis-$W(CO)_4(PPh_2H)_2$ was carried out following the published method.[13] The desired white compound 1.3 g (10 % yield) was obtained (M.P. 87-89 ^0C).

(4) Preparation of Dichloro(cyclooctadiene)palladium, $(COD)PdCl_2$

The preparation of $(COD)PdCl_2$ was carried out following the published method.[16b] The desired orange yellow compound (4.6 g, 87 %) was obtained. It decomposed above 201 ^0C.

(5) Preparation of cis-dichlorobis(diphenylvinylphosphine)-palladium, cis-$(PPh_2CH=CH_2)_2PdCl_2$

Dichloro(cyclooctadiene)palladium (0.57g, 0.002 mole) was introduced into a 200 mL round-bottom flask and a Teflon coated magnetic stirring pea was added, followed by 100 mL of CH_2Cl_2. The flask was immersed halfway in an oil bath and a magnetic stirring unit was placed under

the oil bath. Nitrogen gas was bubbled into the solution through a glass inlet tube for ca. 10 minutes, after which diphenylvinylphosphine, $Ph_2PCH=CH_2$, (0.54 mL, 0.004 mole) was injected directly into the flask by means of a syringe. The reaction was carried out under a nitrogen atmosphere at room temperature for 17 hours. The solvent was then removed by simple vacumm at room temperature. The residue was washed with petrolum ether five times to remove unreacted phosphine and recrystallized from dichloromethane/methanol to give 0.72 g (60 % yield) of the product. It decomposed above 263 ^{0}C.

(6) Preparation of cis-dichlorobis(diphenylphosphine)palladium, cis-$(Ph_2PH)_2PdCl_2$

This complex was prepared by the same procedure as for the cis-$(PPh_2CH=CH_2)_2PdCl_2$complex. A 0.57 g (0.002 mole) sample of dichloro(1-5-η)-cyclooctadiene)palladium was mixed with 0.46 mL (0.004 mole) of diphenylphosphine. The reaction was carried out at room temperature for 18 hours. The product was collected, washed and recrystallized to give 0.42 g of expected product. It decomposed above 225 ^{0}C.

(7) Preparation of cis-dichlorobis(diphenylvinylphosphine)platinum, cis-$Pt(PPh_2CH=CH_2)_2Cl_2$

Potassium tetrachloroplatinate (0.513 g, 1.25 mmole) was introduced into a 100 mL round bottom flask with 30 mL of ethanol to form a heterogeneous mixture. The mixture was purged with nitrogen gas and 0.33 mL (2.5 mmole)

of diphenylvinylphosphine was added with a syringe.

The reaction was carried out at room temperature. The reaction product was washed with petroleum ether two times, followed by drying the compound at 40 ^{0}C under reduced pressure for four hours. A 0.45 g (33 % yield) sample of expected product (M.P. 129-132 ^{0}C) was obtained after two recrystallizations from a dichloromethane/methanol solution.

(8) Preparation of dichlorobis(diphenylphosphine)platinum, $Pt(Ph_2PH)_2Cl_2$.

This complex was prepared by the same procedure as for the cis-dichlorobis(diphenylvinylphosphine)platinum. Potassium tetrachloroplatinate 0.517 g (1.25 mmole), diphenylphosphine 0.29 mL (2.5 mmole) were used and 0.35 g (27 %) of expected product (M.P. 191-193 ^{0}C) was obtained.

(9) Preparation of dichloro(cyclooctadiene)platinum, $(COD)PtCl_2$

The preparation of $(COD)PtCl_2$ was carried out following the published method.[16b] The desired white compound (1.9 g; 84 %) was obtained. It decomposed above 220 ^{0}C.

(10) Preparation of fac-tricarbonyltris(diphenylvinylphosphine)tungsten, fac-$(CO)_3W(PPh_2CH=CH_2)_3$

Tungsten hexacarbonyl (3.5 g, 0.010 mole) diphenylvinylphosphine (6.0 mL, 0.04 mole) and 1.0 g of sodium borohydride in ethanol were used as reactants. The

reaction was carried out as described in the preparation of $W(CO)_4(PPh_2CH=CH_2)_2$. After recrystallization from dichloromethane-methanol a white solid (3.6 g; 45 %) was obtained. The IR and P-31 NMR spectra showed the facial complex was the only product.

C. Preparation of Heterobimetallic Complexes

(1) Preparation of the tungsten-palladium complex, $(CO)_4W(PPh_2CH_2CH_2PPh_2)_2PdCl_2$

Method A:

The complex trans-$W(CO)_4(PPh_2CH_2CH_2PPh_2)_2$ (916 mg, 1.0 mmole) and $PdCl_2(COD)$ (1.1 mg, 1.0 mmole) were introduced into a 500 mL round-bottom flask and 300 mL of CH_2Cl_2 was added. Some of the $PdCl_2(COD)$ remained undissolved. The flask was immersed halfway in an oil bath. The reaction was carried out (with stirring) at room temperature. The solution was reduced to 30 ml with a Buchi evaporator, and 20 ml of n-hexane was added. The solution was concentrated to half its volume and the precipitate which was present was collected. A 0.43 g (38.8 %) sample of product was obtained.

Method B:

A dilute solution of $W(CO)_4(PPh_2CH_2CH_2PPh_2)_2$ 0.575 g (0.5 mmole), was prepared by dissolving it in 800 mL of CH_2Cl_2. Similarly a solution of $Pd(COD)Cl_2$ (0.143 g; 0.5 mmole) in 800 mL of CH_2Cl_2 was prepared. A 10 mL aliquot of each solution was added to a 3000 mL round-bottom

flask which contained 80 mL of CH_2Cl_2. The concentration of both metal complexes after this dilution was 0.0625 mM. The reaction was stirred at room temperature for four hours. An additional 22.2 mL of each solution were added to the flask, and stirred for another four hours. This procedure was repeated every four hours until all of the reactant solutions were mixed. The volume of reactant added to the reaction flask was calculated to always provide an initial concentration of 0.0625 mM. At the end of the reaction no precipitate was present in the clear yellow solution. The solvent was reduced with a rotatory evaporator until ca. 20 mL remained. The precipitate which formed 0.25 g (40 %) was collected. It decomposed above 191 ^{0}C. Calcd. for $C_{32}Cl_2H_{28}O_4P_2PdW$: C, 52.96; H, 3.81; P, 9.76; Cl, 5.58. Found: C,52.08; H, 4.26; P, 9.40; Cl, 5.00.

(2) Preparation of the tungsten-platinum complex, $(CO)_4W(PPh_2Ch_2CH_2PPh_2)_2PtCl_2$

The tungsten-platinum complex was prepared by the same procedure as described for the preparation of the tungsten-palladium complex. A pale yellow compound 0.69 g (68 %) was obtained. The compound decomposed above 185 ^{0}C. Calcd. for $C_{32}Cl_2H_{28}O_4P_2PtW$: C, 49.50; H, 3.57; Pt, 14.36; Cl, 5.22. Found: C, 46.97; H, 3.87; Pt, 15.77; Cl, 6.14.

D. Alternate Approach to The Synthese of Heterobimetallic Complexes

Dry THF (100 mL), $(Ph_2PCH=CH_2)_2PtCl_2$ 0.345 g (0.5 mmole), $W(CO)_4(PPh_2H)_2$ 0.255 g (0.5 mmole) and a Teflon coated magnetic stirring pea were introduced into a 200 mL round-bottom flask. The reaction was carried out under nitrogen gas at 62-65 ^{0}C for two hours. The color of the solution was dark brown. The solvent was removed with a rotatory evaporator and a dark brown compound was obtained. The product, shown to be a mixture by P-31 NMR, did not contain the bimetallic complex sought.

E. Attempted Preparations

(1) Preparation of cis-tetracarbonylbis(diphenylphosphine)tungsten, cis-$W(CO)_4(PPh_2H)_2$.

Tungsten hexacarbonyl (6.0 g, 0.017 mole) was introduced into a 250 mL round-bottom flask containg 120 mL of n-butanol. Sodium borohydride (1.0 g) was added. Nitrogen gas was bubbled into the solution through a gas inlet tube for approximately 10 minutes. During this period, an excess of diphenylphosphine (Ph_2PH) (3.9 mL, 0.034 mole) was injected directly into the flask. The reaction was carried out by refluxing the solution at 120 ^{0}C (obtained with an oil bath) for 9 hours under a nitrogen atmosphere. As the reaction took place the color of the solution changed from colorless to yellow, and finally to red with the formation of a red precipitate. The red product was collected and sublimed to removed the unreacted hexacarbonyl tungsten. The red solid was soluble in halocarbon solvents. Silica gel and an elut-

ing solvent of 90 % petrolum ether/ 10 % ethyl acetate was used in thin layer chromatography to reveal three compounds. The principal product, $W_2(CO)_7(PPh_2)_2(PPh_2H)$ was eluted second, while $W_2(CO)_8(PPh_2)_2$ was eluted first. The compound eluted last was not identified. Separation of these compound was not achieved but identification was possible with P-31 NMR techniques. When this reaction was carried out in ethanol, the same result was obtained.

(2) Preparation of <u>fac</u>-tricarbonyltris[(tetraphenyldiphosphino)ethane]tungsten, <u>fac</u>-$W(CO)_3(PPh_2CH_2CH_2PPh_2)_3$

Into a 250 mL round-bottom flask, dry THF (120 mL) and <u>fac</u>-$W(CO)_3(PPh_2CH{=}CH_2)_3$ (1.0 g, 1.1 mmole) were placed. Nitrogen gas was bubbled through the solution for approximately 10 minutes, and Ph_2PH (0.58 mL, 3.3 mmole) was injected. The reaction was carried out by heating the solution under reflux at 62 ^{0}C for three hours under nitrogen. The solvent was removed and a P-31 NMR spectrum was obtained for the crude product. The expected product, <u>fac</u>-$W(CO)_3(PPh_2CH_2CH_2PPh_2)_3$, could not be identified in the P-31 spectrum. The principal product from this reaction was <u>fac</u>-$W(CO)_3(\eta^2\text{-}PPh_2CH_2CH_2PPh_2)\text{-}(\eta^1\text{-}PPh_2CH_2CH_2PPh_2)$ as shown by P-31 NMR.

Appendix A A computer Code for Simulating NMR Spectra

A large-scale computer system which was located on the campus of Southern Illinois-Edwardsville and belonged to Mid-Illinois Computer cooperative (MICC) was used. The CPU of the computer was CDC Cyber 170/730.

This program was written by using FORTRAN 77 computerlanguage. One can utilized this program by giving data to the computer after each question mark. A simulating spectrum , the relative intensity and chemical shift data can be obtained.

```
00100       PROGRAM P31(INPUT,OUTPUT,SPTRUM1,TAPE5=INPUT,TAPE6=OUTPUT,
00110+      TAPE9=SPTRUM1)
00120       DIMENSION FREQ(64),RINTEN(64),X(20003),Y(20003)
00130       DIMENSION XJX(16),DX(7),MK(16)
00140       DATA XJX,DX/16*0.0,7*0.0/
00150       DATA MK/16*0/
00160       DATA X,Y/20003*0.0,20003*0.0/
00170       DATA FREQ/64*0.0/
00180       DATA RINTEN/64*0.0/
00190       WRITE(6,777)
00200   777 FORMAT(1H,"GIVE THE SPIN SYSTEM")
00210       READ(5,*) N
00220       WRITE(6,778)
00230   778 FORMAT(1H,"GIVE THE INTENSITY OF MAGNETIC FIELD,IN MHZ,
00240+      IF THE CHEMICAL SHIFTS ARE IN HZ NOT IN PPM,PLEASE GIVE
00250+      THIS VALUE AS 1")
00260       READ(5,*) V
00270       WRITE(6,780)
00280   780 FORMAT(1H,"GIVE THE CHEMICAL SHIFTS")
00290       READ(5,*) (DX(KI),KI=1,N)
00300       KN=0
00310       KM=N-1
00320       DO 783 MN=1,KM
00330       MK(MN)=MK(MN)+MN
00340   783 KN=KN+MK(MN)
00350       WRITE(6,781)
00360   781 FORMAT(1H,"COUPLING CONST. ? FOLLOWING:J12,J13,J1N..J(N-1)
00370       READ(5,*) (XJX(KJ),KJ=1,KN)
00380       WRITE(6,779)
00390   779 FORMAT(1H,"GIVE THE SWEEP WIDTH,LARGE TO SMALL")
00400       READ(5,*) T1,T2
00410       WRITE(6,782)
00420   782 FORMAT(1H,"THE RESOLUTION OF INSTRUMENT")
00430       READ(5,*) DEL
00440       WRITE(6,747)
00450   747 FORMAT(1H,"HOW MANY DATA YOU WANT TO COLLECT WITHIN THIS
00460+      SWEEP WIDTH.DO NOT ASK FOR MORE THAN 20000")
00470       READ(5,*) NU
00480       WRITE(6,737)
00490   737 FORMAT(1H,"IF IT'S A 'H SPECTRUM,TYPE 1;IF IT'S A 31P
00500+      SPECTRUM,TYPE 2;IF IT'S A 13C SPECTRUM,TYPE 3")
00510       READ(5,*) NZ
00520       CALL PLOTS(11,111,9)
00530       CALL PLOT(0.0,1.0,-3)
00540       T3=-(T1-T2)/10.0
00550       IF(NZ.EQ.1) GO TO 401
00560       IF(NZ.EQ.2) GO TO 402
00570       CALL AXIS(0.0,-0.25,16H100 MHZ SPECTRUM,
00580+      -16,10.0,0.0,T1,T3)
00590       GO TO 403
00600   402 CALL AXIS(0.0,-0.25,16H100 MHZ SPECTRUM,
00610+      -16,10.0,0.0,T1,T3)
00620       GO TO 403
```

```
00630  401 CALL AXIS(0.0,-0.25,15H60 MHZ SPECTRUM,
00640+     -15,10.0,0.0,T1,T3)
00650  403 CALL CHIPING(FREQ,RINTEN,NY,N,V,XJX,DX)
00660       NU1=NU+1
00670       NU2=NU+2
00680       NU3=NU+3
00690       DO 10 I=1,NU
00700       X(I)=X(I)+T1+(T1-T2)/NU-I*(T1-T2)/NU
00710       DO 30 J=1,NY
00720    30 Y(I)=Y(I)+RINTEN(J)*DEL/(DEL**2+(X(I)-FREQ(J))**2)
00730    10 CONTINUE
00780       X(NU2)=T1
00790       X(NU3)=T3
00800       CALL SCALE(Y,4.0,NU1,1)
00810       CALL LINE(X,Y,NU1,1,0,2)
00820       CALL PLOT(12.0,-5.0,999)
00830       STOP
00840       END
00850       SUBROUTINE CHIPING(FREQ,RINTEN,NY,N,V,XXJ,D)
00860       DIMENSION XM(16,4),H(16,16),XJ(4,4),EG(4),FREQ(64),RINTEN
00870       DIMENSION U(16,16),C(16,16),UC(16,16),CUC2(16,16)
00880       DIMENSION XXJ(16),D(7)
00890       DATA XM/64*1.0/
00900       DATA H/256*0.0/
00910       DATA EG/4*0.0/
00920       DATA U/256*0.0/
00930       DATA C/256*0.0/
00940       DATA CUC2/256*0.0/
00950       DATA UC/256*0.0/
00960       DATA XJ/16*0.0/
00970       K15=0
00980       DO 301 K11=1,N
00990       DO 301 K12=1,N
01000       IF(K11.EQ.K12) GO TO 301
01010       IF(K11.GT.K12) GO TO 303
01020       K15=K15+1
01030       XJ(K11,K12)=XXJ(K15)+XJ(K11,K12)
01040       GO TO 301
01050  303 XJ(K11,K12)=XJ(K12,K11)+XJ(K11,K12)
01060  301 CONTINUE
01070       DO 50 I12=1,N
01080       EG(I12)=V*D(I12)
01090    50 CONTINUE
01100C   DEFINE UNCOUPLED NUCLEAR SPIN SPHERICAL HARMONICS
01110       N1=2**N
01120       DO 100 I13=1,N1
01130       SUM=0.0
01140       XI=I13-1.0
01150       DO 100 J9=1,N
01160       S1=XM(I13,J9)*2**(N-J9)
01170       SUM=SUM+S1
01180       IF(SUM.LE.XI) GO TO 51
01190       XM(I13,J9)=XM(I13,J9)-0.5
```

```
01200       SUM=SUM-S1
01210       GO TO 100
01220    51 XM(I13,J9)=XM(I13,J9)-1.5
01230   100 CONTINUE
01240C   CONSTRUCT HAMILTONIAN MATRIX
01250C   CONSTRUCT TRANSITION DIPOLE MATRIX
01260       L1=1
01270C OFF-DIAGONAL ELEMENTS
01280       DO 102 I16=1,N1
01290       DO 102 J5=1,N1
01300       IF(I16.EQ.J5) GO TO 102
01310       M=0
01320       K7=0
01330       K9=0
01340       C1=0.0
01350       DO 103 I1=1,N
01360       XK=XM(I16,I1)-XM(J5,I1)
01370       XK1=ABS(XK)
01380       IF(XK1.EQ.0.0) GO TO 103
01390       M=M+XK1
01400       IF(M.GT.2) GO TO 102
01410       IF(M.EQ.2) GO TO 200
01420       K7=K7+I1
01430       GO TO 103
01440   200 K9=K9+I1
01450       C1=C1+XJ(K7,K9)
01460   103 CONTINUE
01470       H(I16,J5)=H(I16,J5)+C1/2.0
01480       IF(M.NE.1) GO TO 108
01490       U(I16,J5)=1.0
01500   108 IF(I16.NE.L1.AND.J5.NE.L1.AND.I16.NE.N1.AND.J5.NE.N1)GO TO 1
01510       H(I16,J5)=0.0
01520   102 CONTINUE
01530C   DIAGONAL ELEMENTS
01540       DO 105 I17=1,N1
01550       DO 106 J4=1,N
01560       H(I17,I17)=H(I17,I17)-XM(I17,J4)*EG(J4)
01570   106 CONTINUE
01580       DO 107 J2=1,N
01590       J6=J2+1
01600       DO 107 J1=J6,N
01610       H(I17,I17)=H(I17,I17)+XM(I17,J2)*XM(I17,J1)*XJ(J2,J1)
01620   107 CONTINUE
01630   105 CONTINUE
01700C   JACOBI METHOD----------
01710        CALL HDIAG(H,N1,N1,0,0,C)
01740C -----CALCULATE THE ALLOWED TRANSITION INTENSITY-----
01750        DO 711 I=1,N1
01760        DO 711 J=1,N1
01770        DO 711 K=1,N1
01780        UC(I,J)=UC(I,J)+U(I,K)*C(K,J)
01790    711 CONTINUE
01800        DO 712 I=1,N1
```

```
01810         DO 712 J=1,N1
01820         DO 713 K=1,N1
01830         CUC2(I,J)=CUC2(I,J)+C(K,I)*UC(K,J)
01840    713 CONTINUE
01850         CUC2(I,J)=CUC2(I,J)**2
01860    712 CONTINUE
01870C   ------CALCULATE THE SPECTRUM----------------------
01880         NY=0
01890         N3=N1-1
01900         DO 700 I=1,N3
01910         IN=I+1
01920         DO 700 J=IN,N1
01930         IF(CUC2(I,J).EQ.0.0) GO TO 700
01940         NY=NY+1
01950         E1=H(I,I)-H(J,J)
01960         FREQ(NY)=ABS(E1)
01990         RINTEN(NY)=CUC2(I,J)
02020    700 CONTINUE
02030         RETURN
02040         END
02050        SUBROUTINE HDIAG(A,N,NDIM,IEGEN,IORD,EIVR)
02060C
02070C
02080C
02090C A=MATRIX TO BE DIAGONALIZED
02100C NDIM=DIMENSION OF A
02110C N=DIMENSION OF SUBMATRIX TO BE DIAGONALIZED
02120C IEGEN=0 IF BOTH EIGENVALUES AND EIGENVECTORS ARE DESIRED
02130C         1 IF ONLY EIGENVALUES ARE DESIRED
02140C IORD=0 IF NO ORDERING OF EIGENVALUES OR VECTORS IS DESIRED
02150C           (ORDER IN = ORDER OUT)
02160C         1 IF ORDERING BY SIZE OF EIGENVALUES IS DESIRED
02170C EIVR=TRANSFORMATION MATRIX (MATRIX OF EIGENVECTORS)
02180C
02190C*****THIS ROUTINE USES A VARIABLE THRESHOLD JACOBI METHOD
02200C*****IT GIVES VERY GOOD EIGENVALUES AND EIGENVECTORS
02210C*****THE ROUTINE IS MUCH FASTER THAN THE OLD HDIAG ROUTINE WRITT
02220C*****AT M.I.T. THAT USES THE JACOBI METHOD BUT NOT THE VARIABLE
02230C*****THRESHOLD TECHNIQUE THAT IS APPLIED HERE
02240C
02250        DIMENSION A(NDIM,NDIM),EIVR(NDIM,NDIM)
02260        IF(N.GT.0) GOTO 1
02270        EIVR(1,1)=1.0
02280        RETURN
02290      1 IF(IEGEN.GT.0) GO TO 102
02300        DO 101 J=1,N
02310        DO 100 I=1,N
02320    100 EIVR(I,J)=0.0
02330    101 EIVR(J,J)=1.0
02340C          FIND THE ABSOLUTELY LARGEST ELEMENT OF A
02350    102 ATOP=0.
02360        DO 111 I=1,N
02370        DO 111 J=I,N
```

```
      IF(ATOP.GE.ABS(A(I,J)))  GO TO 111
      ATOP=ABS(A(I,J))
  111 CONTINUE
      IF(ATOP)109,109,113
  109 RETURN
C        CALCULATE THE STOPPING CRITERION -- DSTOP
  113 AVGF=FLOAT(N*(N-1))*.55
      D=0.0
      DO 114 JJ=2,N
      DO 114 II=2,JJ
      S=A(II-1,JJ)/ATOP
  114 D=S*S+D
      DSTOP=(1.E-06)*D
C        CALCULATE THE THRESHOLD, THRSH
C
      THRSH=SQRT(D/AVGF)*ATOP
C
C        START A SWEEP
C
  115 IFLAG=0
      DO 130 JCOL=2,N
      JCOL1=JCOL-1
      DO 130 IROW=1,JCOL1
      AIJ=A(IROW,JCOL)
C
C        COMPARE THE OFF-DIAGONAL ELEMENT WITH THRSH
C
      IF(ABS(AIJ).LE.THRSH)  GO TO 130
      AII=A(IROW,IROW)
      AJJ=A(JCOL,JCOL)
      S=AJJ-AII
C
C        CHECK TO SEE IF THE CHOSEN ROTATION IS LESS THAN THE ROUNDING ERRO
C        IF SO, THEN DO NOT ROTATE.
C
      IF(ABS(AIJ).LE.(1.0E-09*ABS(S)))   GO TO 130
      IFLAG=1
C
C        IF THE ROTATION IS VERY CLOSE TO 45 DEGREES, SET SIN AND COS
C        TO 1/(ROOT 2).
C
      IF((1.0E-10*ABS(AIJ)).LT.ABS(S)) GO TO 116
      S=.7071067810
      C=S
      GO TO 120
C
C        CALCULATION OF SIN AND COS FOR ROTATION THAT IS NOT VERY CLOSE
C        TO 45 DEGREES
C
  116 T=AIJ/S
      S=0.250/SQRT(0.250+T*T)
C
C        COS = C ,  SIN= S
```

```
02910C
02920       C=SQRT(0.500+S)
02930       S=2.00*T*S/C
02940C
02950C          CALCULATION OF THE NEW ELEMENTS OF MATRIX A
02960C
02970   120 DO 121 I=1,IROW
02980       T=A(I,IROW)
02990       U=A(I,JCOL)
03000       A(I,IROW)=C*T-S*U
03010   121 A(I,JCOL)=S*T+C*U
03020       I2=IROW+2
03030       IF(I2.GT.JCOL) GO TO 123
03040       DO 122 I=I2,JCOL
03050       T=A(I-1,JCOL)
03060       U=A(IROW,I-1)
03070       A(I-1,JCOL)=S*U+C*T
03080   122 A(IROW,I-1)=C*U-S*T
03090   123 A(JCOL,JCOL)=S*AIJ+C*AJJ
03100       A(IROW,IROW)=C*A(IROW,IROW)-S*(C*AIJ-S*AJJ)
03110       DO 124 J=JCOL,N
03120       T=A(IROW,J)
03130       U=A(JCOL,J)
03140       A(IROW,J)=C*T-S*U
03150   124 A(JCOL,J)=S*T+C*U
03160C
03170C          ROTATION COMPLETED.
03180C          SEE IF EIGENVECTORS ARE WANTED BY USER
03190C
03200       IF(IEGEN.GT.0) GO TO 126
03210       DO 125 I=1,N
03220       T=EIVR(I,IROW)
03230       EIVR(I,IROW)=C*T-EIVR(I,JCOL)*S
03240   125 EIVR(I,JCOL)=S*T+EIVR(I,JCOL)*C
03250C
03260C          CALCULATE THE NEW NORM D AND COMPARE WITH DSTOP
03270C
03280   126 CONTINUE
03290       S=AIJ/ATOP
03300       D=D-S*S
03310       IF(D.GE.DSTOP) GOTO 129
03320C
03330C          RECALCULATE DSTOP AND THRSH TO DISCARD ROUNDING ERRO
03340C
03350       D=0.00
03360       DO 128 JJ=2,N
03370       DO 128 II=2,JJ
03380       S=A(II-1,JJ)/ATOP
03390   128 D=S*S+D
03400       DSTOP=(1.E-06)*D
03410   129 THRSH=SQRT(D/AVGF)*ATOP
03420   130 CONTINUE
03430       IF(IFLAG.NE.0) GOTO 115
```

```
03440C
03450C      ARRANGE THE EIGENVALUES IN THE ORDER OF INCREASING ENERGY.
03460C      ARRANGE THE EIGENVECTORS IN THE SAME ORDER.
03470C
03480       IF(IORD.EQ.0) RETURN
03490       NU=N
03500       DO 11 I=1,N
03510       IF(I.GE.NU)    RETURN
03520       AMIN=A(I,I)
03530       DO 10 J=I,NU
03540       IF(A(J,J).GE.AMIN)    GO TO 10
03550C      IF EIGEN IS -1 , EXCLUDE UNCONVERGED EIGENVALUES FROM ORDER
03560       TE=ABS(EIVR(N,J))+ABS(EIVR(N-1,J))
03570       IF((TE.GT..05).AND.(IEGEN.EQ.-1))    GO TO 15
03580       II=I
03590       AMIN =A(J,J)
03600       A(J,J)=A(I,I)
03610       A(I,I)=AMIN
03620    16 DO 12 K=1,N
03630       TEMP=EIVR(K,II)
03640       EIVR(K,II)=EIVR(K,J)
03650    12 EIVR(K,J)=TEMP
03660       GO TO 10
03670    15 AM=A(J,J)
03680       A(J,J)=A(NU,NU)
03690       A(NU,NU)=AM
03700       II=NU
03710       NU=NU-1
03720       GO TO 16
03730    10 CONTINUE
03740    11 CONTINUE
03750       RETURN
03760       END

 READY.
```

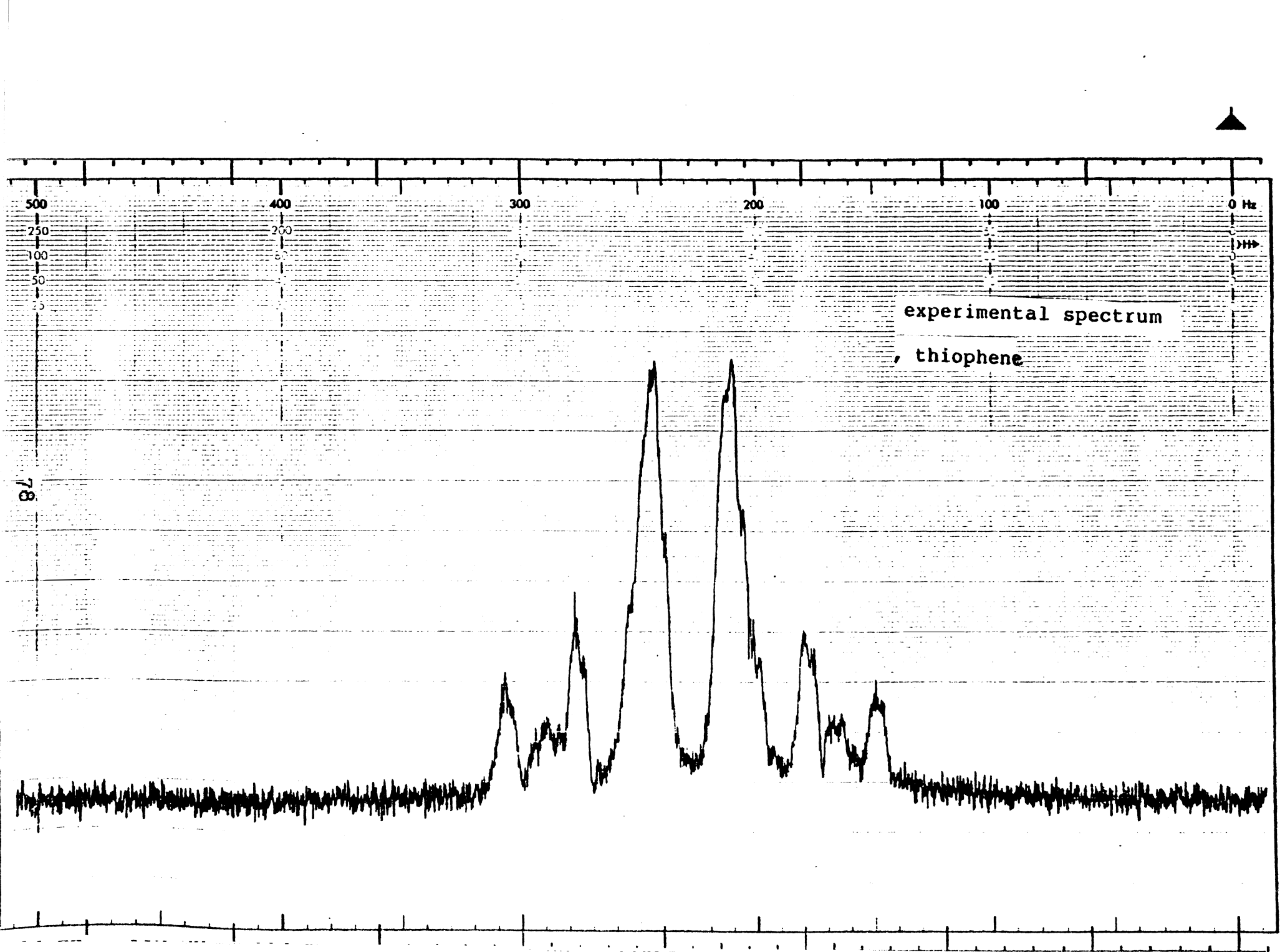
** : It was used under the permission from Dr. Giles Henderson, the author.

Appendix B

The Comparison Between Experimental NMR Spectra and Simulating NMR Spectra of Some Known Compounds

One experimental spectrum or published spectrum* and one simulated spectrum of the three compounds: 1,2-dichloro-3,4,5,6-tetrafluorobenzene, thiophene, and 2,6-dimetnoxyphenol, are given in this appendix. The experimental spectra were obtained by using a Varian T-60 NMR spectrometer. The simulated spectra were calculated by computer with published constants of those three compounds.*

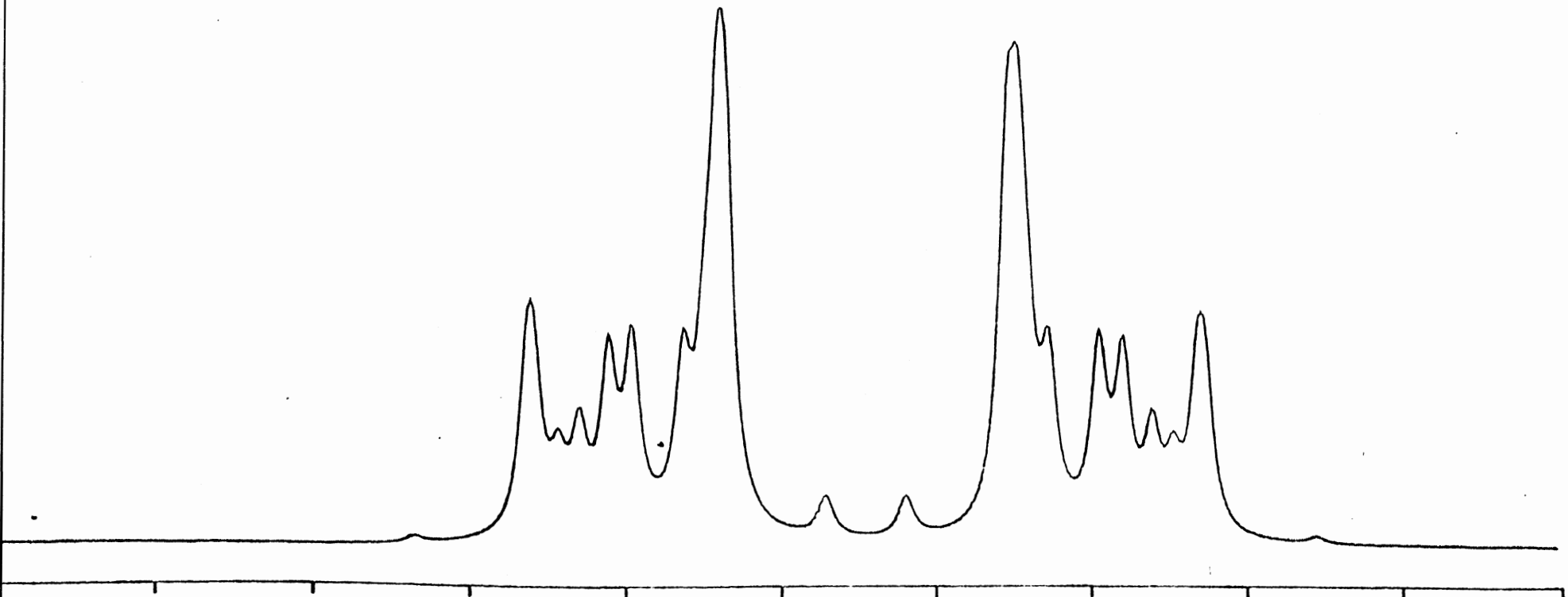
*: J. W. Emsley, J. Feeney and L. H. Sutcliffe; High Resolution Nuclear Magnetic Resonance Spectroscopy, (Pergamon Press Ltd.London, 1967)


500
400
300
200
100
0 Hz
250
200
100
50
25
experimental spectrum
, thiophene

simulating spectrum

thiophen δ_{ab} = 14.61 Hz J_{ab} = 5.00 Hz

$J_{ab'}$ = 1.06 Hz $J_{aa'}$ = 3.50 Hz $J_{bb'}$ = 2.80 Hz



60 MHZ SPECTRUM

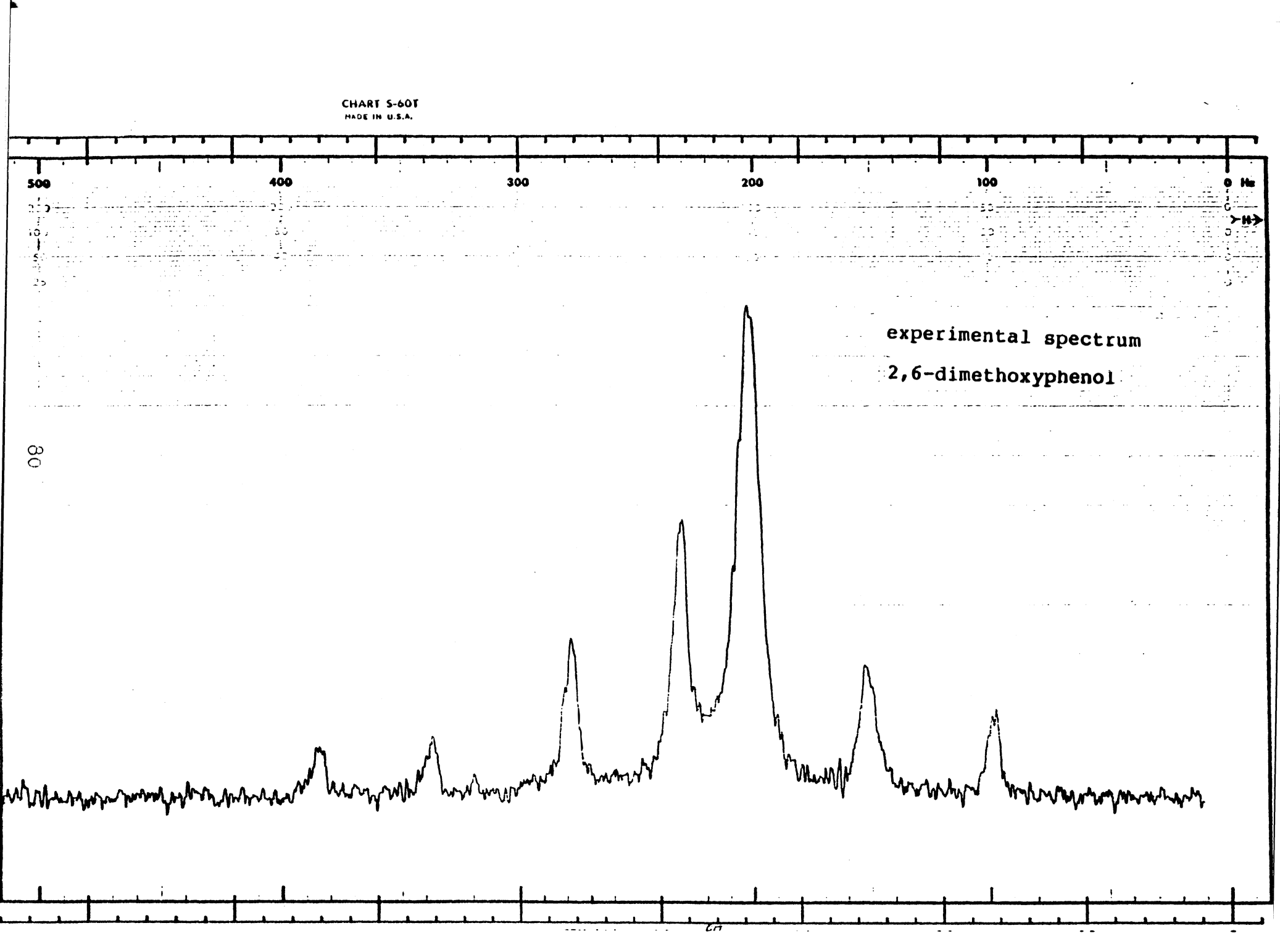
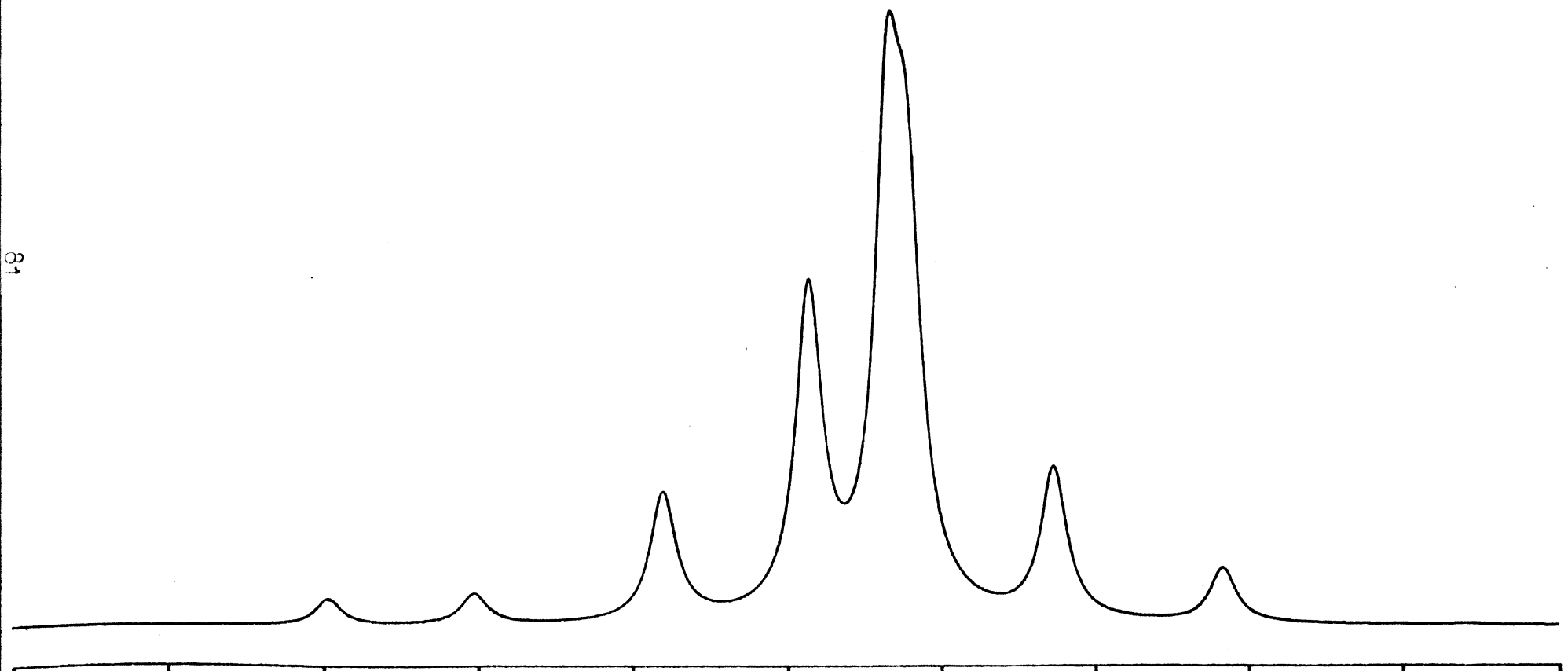


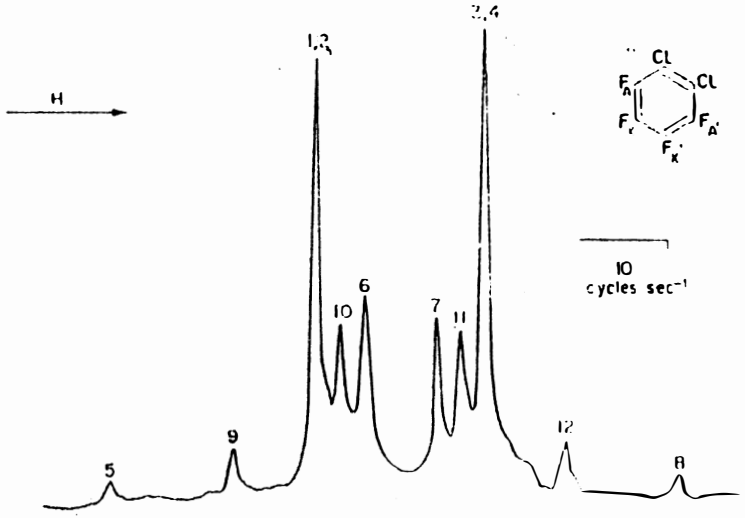
CHART S-60T
MADE IN U.S.A.
500
400
300
200
100
0 Hz
experimental spectrum
2,6-dimethoxyphenol
80

simulating spectrum



60 MHZ SPECTRUM

2,6-dimethoxyphenol δ_{ab} = 10 Hz J_{ab} = 8.6 Hz



The low field part (AA' fluorine nuclei) of the ^{19}F resonance spectrum of neat 1,2,-dichloro-3,4,5,6-tetrafluorobenzene.*

a literature spectrum

1,2-dichloro-3,4,5,6-tetrafluorobenzene

simulating spectrum

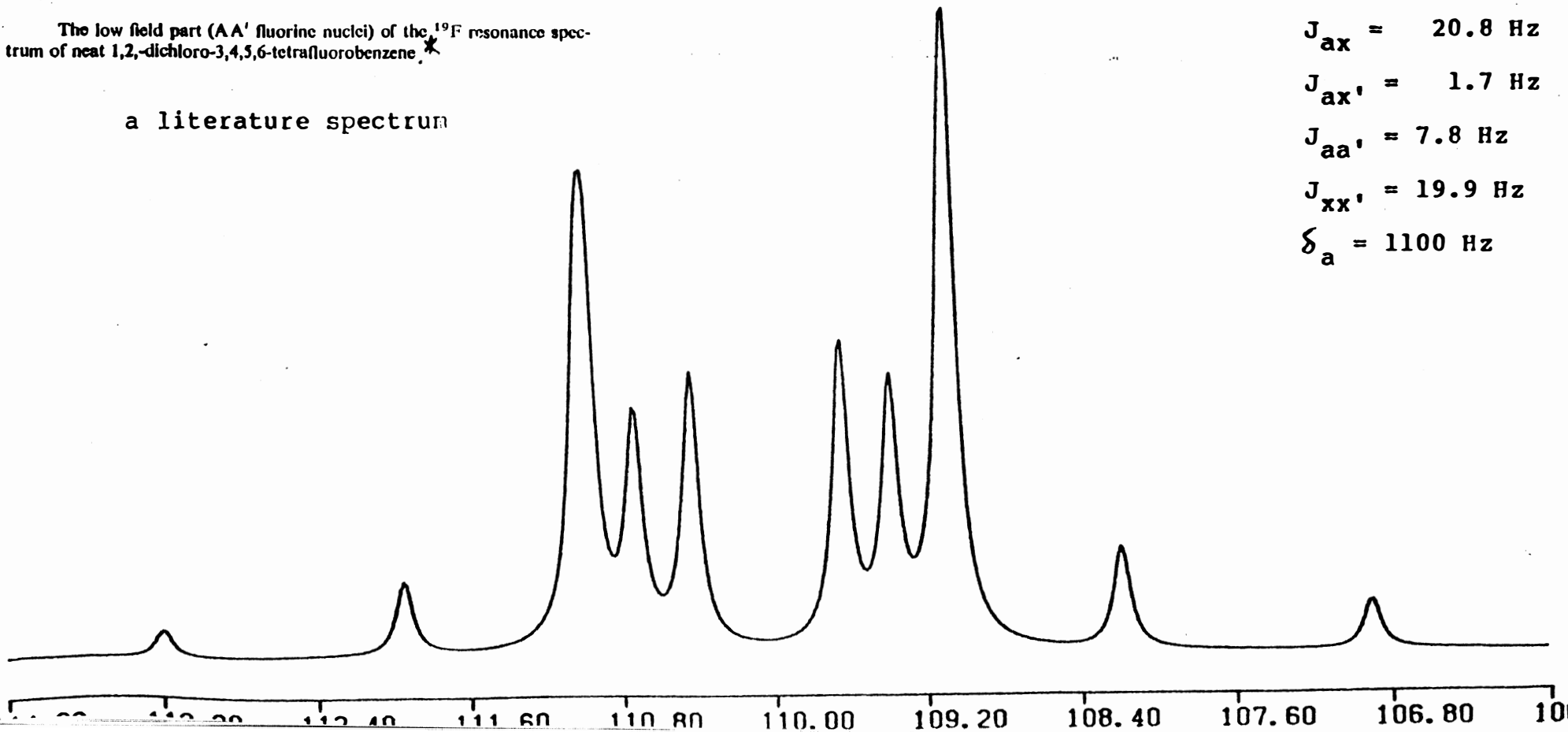
J_{ax} = 20.8 Hz

$J_{ax'}$ = 1.7 Hz

$J_{aa'}$ = 7.8 Hz

$J_{xx'}$ = 19.9 Hz

δ_a = 1100 Hz



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